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Lithium Nickel Cobalt Manganese Oxide Synthesized Using Alkali Chloride Flux: Morphology and Performance As a Cathode Material for Lithium Ion Batteries

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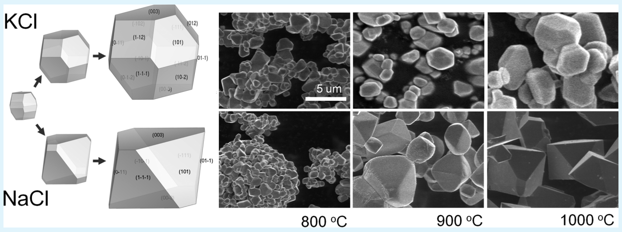
Supporting Information

ABSTRACT: $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$ (NCM811) was synthesized using alkali chlorides as a flux and the performance as a cathode material for lithium ion batteries was examined. Primary particles of the powder were segregated and grown separately in the presence of liquid state fluxes, which induced each particle to be composed of one primary particle with well-developed facet planes, not the shape of agglomerates as appears with commercial NCMs. The new NCM showed far less gas emission during high temperature storage at charged states, and higher volumetric capacity thanks to its high bulk density. The material is expected to provide optimal performances for pouch type lithium ion batteries, which require high volumetric capacity and are vulnerable to deformation caused by gas generation from the electrode materials.



KEYWORDS: *lithium nickel cobalt manganese oxide, flux, particle morphology, gas generation, lithium ion battery*

INTRODUCTION

Lithium ion battery (LIB) is widely used as a power source for mobile electronic devices because of its high energy density.[1−3] Recently, various size and shape of batteries are being developed because new mobile devices such as cell phones and tablet PCs require batteries suitable for their specific design. And electric vehicles started adopting LIBs. Because of these trends, demands for pouch type cells whose shape and dimension can be flexibly designed are increasing.

Lithium nickel oxide ($LiNiO_2$; LNO) is a promising alternative to $LiCoO_2$ (LCO) which is widely used in lithium ion batteries.[4−6] LNO is isostructural with LCO, whose crystal structure consists of layers of transition metal cations separated from Li layers by oxygen and which belongs to the space group $R\bar{3}m$.[7−10] LNO has a higher specific energy, is less toxic, and the raw materials are less expensive.[11−15] Because it is well-known that substitution of part of Ni with Co and/or Mn improves structural and thermal stability of the material, several composition of $Li(Ni_{1-x-y}Co_xMn_y)O_2$ (NCM) have been developed and commercially available now.[16−19] NCM with 5:2:3 ratio of Ni, Co, and Mn (NCM523) is commercialized in particular, because it shows reasonable performances of capacity, stability, and safety.

The most significant problem of commercial NCM is emission of a lot of gas at charged states. Pouch type polymer cells are easily deformed with gas evolution from the electrodes, and this is a main problem in the industrial production. It is reported that oxygen emitted from charged cathode reacts with electrolytes and this generates gas.[20−22] Although it is not clear why NCM generates more gas than LCO does, particle morphology seems to be one of the main factors. Particles of commercial LCO are generally composed of single primary body, whereas typical NCM particles are in a shape of agglomerates composed of many primary crystals (Figure 1a). Larger surface area of NCM may cause more reaction with electrolytes.

In this study, NCM was synthesized with use of KCl or NaCl fluxes, which induces growth of primary particles and makes each particle in a shape of a single body, not the shape of agglomerates.[23] The 811-composition is chosen in this study to secure capacity margin considering the loss occurring with flux process. Performance of NCMs as a cathode material of LIBs are investigated in the relation with the particle morphology, and compared with those of commercial NCM523. On the basis of the results, we discuss that the new NCM of this study is cut out for pouch type polymer LIBs adopting Si-based anodes.

RESULTS AND DISCUSSION

Figure 1a shows the SEM image of commercial NCM which is usually synthesized from hydroxide precursors (Figure 1e). Commercial NCM particle maintains spherical outline of the precursor in general, and each particle is composed of small primary crystals. The agglomerate disjointed and the primary

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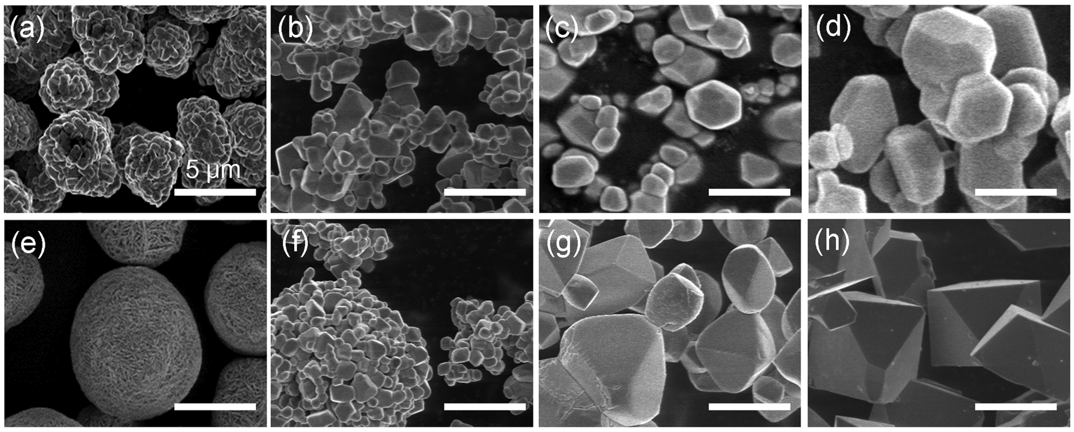

Figure 1. SEM images of NCM synthesized with flux: (b) fired with KCl as a flux at 800 °C (KCl/800 °C), (c) KCl/900 °C, (d) KCl/1000 °C, (f) NaCl/800 °C, (g) NaCl/900 °C, and (h) NaCl/1000 °C. The images of (a) commercial NCM523 and (e) hydroxide coprecipitate used as a precursor are also presented for a comparison.

particles grew separately when KCl (Figure 1b–d) or NaCl (Figure 1f–h)) was used as a flux. The sample fired at 800 °C with NaCl flux (NaCl/800 sample) was the only exception: the particles are still agglomerate of primary crystals, similar shape to commercial NCM. This may be due to higher melting temperature of NaCl than KCl. KCl, whose melting point is 770 °C, exists as a liquid at the synthesis temperature of this study (800–1000 °C), whereas the melting point of NaCl is 801 °C. Therefore, NaCl may have not fully melted at 800 °C . It seems that NaCl/800 sample has similar particle shape to that of commercial NCM for this reason. The results indicate that liquid phase flux separates primary particles of the agglomerate and expedites separate growth of each primary particle.

Particle size increased with increase of firing temperature for both fluxes, but the particle shape developed differently. Particles grown with KCl flux showed more isotropic shape than those grown with NaCl: for example, particles of KCl/1000 sample are round with vague facets, whereas those of NaCl/1000 are in a shape of an octahedron and the facets clearly appear. Our previous study (to be published) of density functional theory showed that the surface of $LiNiO_2$-based cathode materials has the lowest surface energy when the surface is composed of (0 0 3), (1 0 4), (1 −1 −1), and their equivalent facet planes of $\overline{3}m$ point symmetry (see the Supporting Information, S1).

Isotropic shape of the particles grown with KCl may appear because the surface includes additional (0 1 2) and equivalent facets as shown in Figure 2(up). Use of KCl as a flux seems to reduce difference of the surface energy among the facets, resulting in disappearance of the specific octahedral crystal shape. Whereas, NaCl flux made well developed (0 0 3)- and (1 −1 −1)-equivalent facet planes probably because they are more stable than other facets in the existence of liquid NaCl. The morphological character seems to originate from different energy of interfaces between liquid phase of chlorides and the crystal surface, depending on the flux used and crystallographic orientation of the facets. However, more systematic investigation of interfacial energy may be necessary to fully explain the mechanism of particle shape development.

Increasing heating temperature without using chloride flux also increased the size of primary particles. However, this resulted in irregular particle shape, and additional pulverization process was required because the particles were severely agglomerated. This generated unstable fracture surfaces and a lot of fine particles which degrade performance of the cathode (see the Supporting Information, S2). Thus, using chloride flux was advantageous in controlling particle morphology over only changing the heating temperature of simple solid-state reactions.

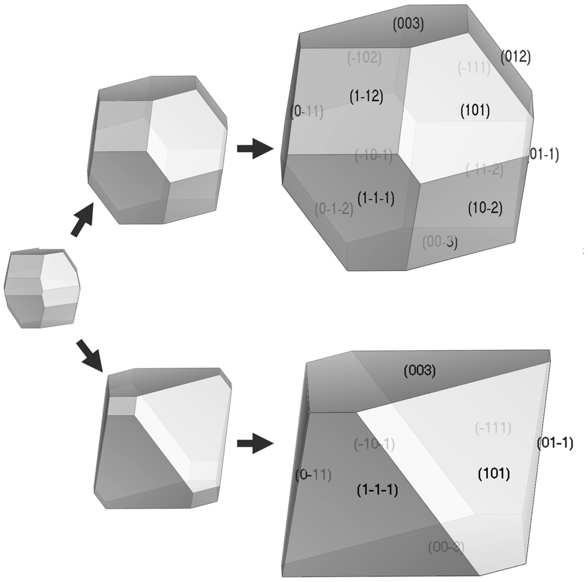

Figure 2. Schematic of crystal growth of NCM with KCl (up) and NaCl (down) fluxes.

Charging/discharging capacity, which was measured with 2016 type coin half cells, decreased with increase in firing temperature of the samples regardless of the fluxes used. Samples fired with NaCl flux showed a little higher capacity than those with KCl at the same temperatures, but the difference was negligible. Charging/discharging profile of the samples synthesized at 900 and 1000 °C are presented in Figure 3. The capacity of the samples fired at 900 °C was comparable to that of commercial NCM523: the charging capacity was a little larger, and the discharging capacity slightly fell short. The capacity of samples synthesized at 1000 °C was too small to be practically used. Samples fired at 800 °C had higher capacity, but they were not considered seriously in this study because they showed little improvement of gas emission

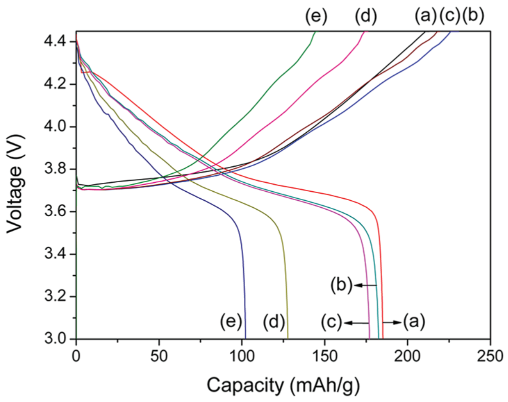

Figure 3. Charging/discharging profile of the coin half cells (at 0.1C rate of commercial NCM): (a) commercial NCM523, (b) NCM fired with NaCl as a flux at 900 °C (NaCl/900 °C), (c) KCl/900 °C, (d) NaCl/1000 °C, and (e) KCl/1000 °C.

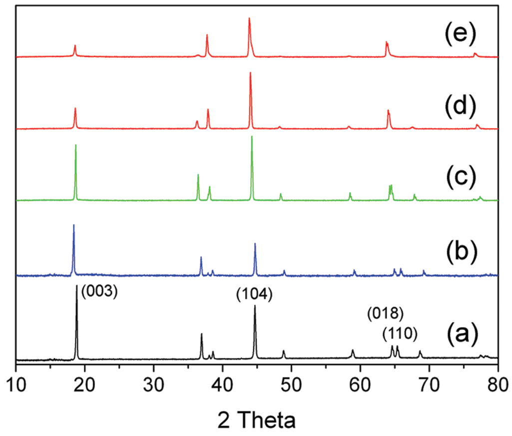

Figure 4. XRD patterns: (a) commercial NCM523, (b) NCM fired with NaCl as a flux at 800 °C (NaCl/800 °C), (c) NaCl/900 °C, (d) NaCl/1000 °C, and (e) KCl/1000 °C.

Figure 4 shows change of XRD pattern with respect to firing temperature. All the samples fired at 800−1000 °C appear to have the same crystal structure with commercial NCM, but quality of crystal declined with increase of the temperature. It is generally accepted that high intensity ratio of (0 0 3)/(1 0 4) peaks and clear separation between (0 1 8) and (1 1 0) peaks are indicators of crystal quality.[24] The (0 0 3)/(1 0 4) ratio decreased and (0 1 8) and (1 1 0) peaks merged with increase of the temperature, which indicates disordering among Li and transition metals increased. This behavior also appeared with simple solid state reaction that does not use any flux (see the Supporting Information, S2). In a previous work,[25] we reported that low chemical potential of oxygen at high temperatures induces vacancies of Li and O in $LiNiO_2$-based crystals. Ni easily diffuses into vacant Li sites and fills them at such conditions, resulting in increase of irregular arrangement of cations. On the basis, it seems that charging/discharging performance dropped with higher synthesis temperatures because perfectness of the crystal structure decreased. The result indicates that though flux-growth in high temperatures enables to get morphological merits, this sacrifice some of the capacity. This capacity loss should be considered designing new cathode materials using the flux-growth method. This is why the 811-composition is chosen to replace NCM523 in this study, that is, in order to secure capacity margin by applying higher Ni-content of NCM.

The measurement results of gas evolution during high temperature storage of charged electrodes are presented in Figure 5, which show that high temperature synthesis with chloride flux is effective reducing gas emission. It is reported that H_2O, CO, CO_2, and hydrocarbons are generated from the decomposition of electrolyte on the surface of charged cathode.[20] Therefore, it is expected that gas-generating chemical reaction would be promoted as surface area of cathode material increases. Surface coating or increase of primary particle size was effective for reduction of gas evolution in our experiments (see the Supporting Information, S3), which supported that controlling interfacial area between cathode material and electrolyte is a key factor for reducing gas generation. NCM particles obtained by flux process at high temperatures are composed of one large primary particles, and samples fired over 900 °C with NaCl have well-developed facet planes in particular. It seems that emission of gas is greatly reduced because this particle shape has much smaller surface area. This interpretation was supported by measurement of the surface area by BET method, which showed surface area of NaCl/900 is much smaller than that of commercial NCM (0.47 and 0.64 m^2/g, respectively).

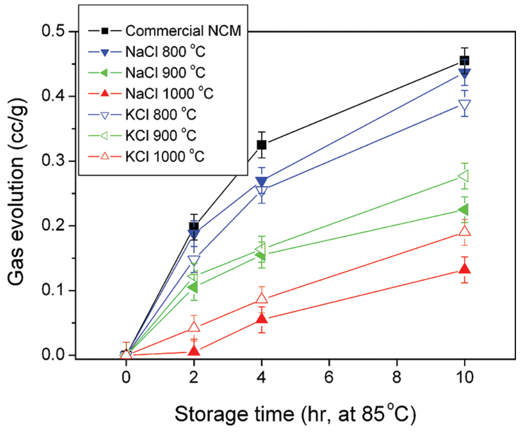

Figure 5. Evolution of gas (cc/gram of NCM) from charged electrodes (4.45 V) with respect to storage time at 85 °C.

Properties of NaCl/900 sample are summarized in Table 1 in comparison with those of commercial NCM523, for we concluded NaCl/900 sample is appropriate for practical use: it showed far less gas emission and comparable electrochemical capacity compared with commercial NCM523. Gravimetric charging capacity of NaCl/900 was a little higher than

Table 1. Comparison of Properties between Commercial NCM523 and NCM of This Study Fired with NaCl Flux at 900 °C

	commercial NCM	NaCl 900 °C
gravimetric charging capacity (mAh/g)	206	215
gravimetric discharging capacity (mAh/g)	182	176
density (g/cm^3)	4.65	4.83
volumetric charging capacity (m Ah/cc)	957	1039
volumetric discharging capacity (mA h/cc)	846	853
gas evolution (storage at 85 °C 10 h, cc/g)	0.46	0.21

commercial NCM523, but the discharging capacity was slightly lower. The ratio of discharging capacity to charging capacity, which is often called discharging/charging efficiency, is an important factor designing lithium ion batteries. It is desirable that the cathode and anode have similar efficiency to offset irreversible capacity loss of each other and minimize any surplus of cathode or anode. We think higher charging capacity and larger irreversibility of NaCl/900 may be another merit because it is suitable for LIBs adopting Si-based anodes which have higher irreversibility than conventional graphite anodes. Of course, improving efficiency of Si-anodes would be necessary, but current commercial Si-based materials have still lower efficiency than C-based ones (see the Supporting Information, S4), thus NaCl/900 may match up with Si-based anodes.

Bulk density measured by liquid pycnometer method is also presented in Table 1. NaCl/900 has higher bulk density (4.8 g/cm^3) than commercial NCM523 (4.6 g/cm^3), probably because particles of NaCl/900 have no inner boundaries while commercial NCM is in a shape of agglomerate which contains spaces among primary particles. Some of the space may exist as closed pores, resulting in decrease of bulk density. The volumetric capacity (mAh/cc), which is an important property designing LIBs, was assessed in a simple way by multiplying gravimetric capacity and bulk density (Table 1). Although NaCl/900 showed slightly lower gravimetric discharging capacity than commercial NCM523 as mentioned above, volumetric capacity of it was superior for both charging and discharging owing to its high bulk density.

It may have to be discussed that composition of the samples in this study (NCM811: the exact composition of NaCl/900 sample analyzed by ICP-OES was $Li_{1.02}Ni_{0.78}Co_{0.12}Mn_{0.10}$) is different from NCM523. Comparison of performances between samples of this study and commercial NCM523 may seem to be unreasonable, because higher gravimetric capacity can be obtained with increase of Ni-content of NCMs. However, amount of gas emission rapidly increases with increase of Ni-content and this has been the main obstacle that blocks practical use of Ni-rich compositions. The main purpose of this study is providing cathode materials with less gas generation than commercial NCM523, with comparable electrochemical performance. The high temperature flux process of this study was effective controlling particle morphology, but it accompanied capacity loss comparing with conventional solid-state reaction, therefore samples of 523-composition synthesized with flux could not provide enough capacity to replace commercial NCM523. We chose 811-composition for this reason, to secure capacity margin considering the loss. In brief, the main achievement of this study may be that gas evolution could be greatly reduced with securing enough capacity.

In summary, we synthesized NCM of 811-composition using alkali chloride fluxes. Each NCM particle could grow separately in the presence of the liquid phase flux. Therefore, particle shape of single body, not the shape of agglomerates as appears with commercial NCM, could be obtained. Owing to this particle shape, the NCM of this study showed less than half the gas evolution of commercial NCM523. This property is expected to solve the swelling and the related performance degradation problems of pouch type LIBs. New NCM of this study provides larger volumetric capacity than commercial NCM523 owing to its high bulk density, and it is suitable for LIBs which use Si-based anodes because of its high charging capacity and irreversibility. Reduction of raw material cost is another merit because we used the 811-composition which contains less Co than commercial 523-composition. Thus, the new NCM is expected to be a good alternative to conventional cathode materials in the application of pouch type LIBs whose market is growing rapidly.

■ EXPERIMENTAL SECTION

The coprecipitate $(Ni_{0.8}Co_{0.1}Mn_{0.1})(OH)_2$ was obtained by a continuous coprecipitation method[25,26] and was used as the precursor. The hydroxide precursors were mixed with LiOH-H_2O (99%, Samchun chemical Ltd., Korea). The Li/TM molar ratio of mixing was fixed at 1.10 considering evaporation loss of Li. The mixture of raw materials was again mixed with KCl or NaCl in the weight ratio of 1:3, and heated at 800, 900, and 1000 °C for 10 h under a flow of dry air (40 L/min). The sintered body was dispersed and washed in deionized water. Because the chloride fluxes have high solubility in water, they could be easily removed by repeated washing and filtering processes. After drying at 120 °C, the powder was again annealed at 750 °C for 10 h to remove residual water on the surface and intercalated in the crystal. The morphology of particles was analyzed using a field-emission scanning electron microscope (FESEM; JEOL, 6360F, Japan), and the surface area was measured by BET method (Micromeritics, ASAP2020, USA). Crystal quality of the samples was analyzed by powder X-ray diffraction (XRD; Rigaku, D-max 2500, Japan). Bulk density of the powders was measured using liquid pycnometer method.

For measurement of the charging/discharging capacity, a coin-type half cell (2016 type) was made. The cathode contained 95 wt % of NCM, 2.5 wt % of carbon black and 2.5 wt % of polyvinylidene fluoride (PVDF, SOLEF6020, Solvay-Solexis, Belgium). An electrolyte solution of 1.15 M $LiPF_6$ in ethyl carbonate/dimethyl carbonate/ethyl methyl carbonate (3:3:4 volume ratio) was used. The charge–discharge profiles of the coin cells were obtained in the voltage range of 4.45–3.0 V with 0.1C current rate of NCM523. The cathode obtained by disassembling charged cells were rinsed with dimethyl carbonate and dried at 60 °C. They were placed in a pouch with fresh electrolyte solution and the pouch was sealed in a vacuum chamber. The pouch was stored at 85 °C, and the volume change with time was measured by liquid pycnometer method to assess the amount of evolved gas.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Determination of face indices, morphology, and XRD of solid-state reaction products, effect of primary particle size and surface coating on gas evolution, charging/discharging profile of commercial Si-SiO_2 composite, and SEM image of commercial NCM. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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