



## Preparation of spherical $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ lithium-ion cathode material by continuous co-precipitation

K.K. Cheralathan<sup>a</sup>, Na Young Kang<sup>a</sup>, Hun Su Park<sup>a</sup>, You Jin Lee<sup>a</sup>, Won Choon Choi<sup>a</sup>,  
Young Soo Ko<sup>b</sup>, Yong-Ki Park<sup>a,\*</sup>

<sup>a</sup> Division of Advanced Chemical Technology, Korea Research Institute of Chemical Technology, Daejeon 305-343, Republic of Korea

<sup>b</sup> Department of Chemical Engineering, Kongju National University, 182 Shingwan-dong, Gongju, Cheungnam 314-701, Republic of Korea

### ARTICLE INFO

#### Article history:

Received 8 June 2009

Received in revised form 11 August 2009

Accepted 25 August 2009

Available online 16 September 2009

#### Keywords:

Lithium battery

Cathode

Continuous co-precipitation

Capacity retention

### ABSTRACT

Micro-spherical  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursors with a narrow size-distribution and high tap-density are prepared successfully by continuous co-precipitation of the corresponding metal salt solutions using NaOH and  $\text{NH}_4\text{OH}$  as precipitation and complexing agents.  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  is then prepared as a lithium battery cathode from this precursor by the introduction of  $\text{LiOH}\cdot\text{H}_2\text{O}$ . The pH and  $\text{NH}_3$ :metal molar ratio show significant effects on the morphology, microstructure and tap-density of the prepared  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  and the  $R$  values and  $I(003)/I(104)$  ratio of lithiated  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ . Spherical  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  prepared under optimum conditions reveals a hexagonally ordered, layered structure without cation mixing and an initial charging capacity of  $176\text{mAhg}^{-1}$ . More than 91% of the capacity is retained after 40 cycles at the 1 C rate in a cut-off voltage range of 4.3–3.0 V.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

Lithium nickel oxide ( $\text{LiNiO}_2$ ) with a layered structure has been studied extensively as an alternative cathode material for rechargeable lithium-ion batteries to replace expensive and toxic lithium cobalt oxide ( $\text{LiCoO}_2$ ) that is presently used. Commercial application has not been achieved, however, due to difficulties in preparation and property control. It is difficult to introduce a stoichiometric amount of Ni (Li:Ni atomic ratio of 1) into  $\text{LiNiO}_2$  particles without any divalent nickel in lithium sites. Also, severe capacity fading is observed on repeated charging and discharging cycles, because the structure stability is lower than that of  $\text{LiCoO}_2$  [1–5]. To circumvent these problems, several types of structure stabilizers, such as transition metals (Co, Mn, Ti, Fe and Zr) and non-transition metals (Mg and Al), have been suggested [6–15]. Among the various stabilizers, cobalt has been shown to hold promise, because it can be substituted in the Ni sites and forms a solid solution of any percentage without affecting the layered structure of  $\text{LiNiO}_2$ . Cobalt modified stabilizers have been found to exhibit enhanced structure stabilization, extended cycleability, and improved charging capacity [16–19]. Nevertheless, the replacement of Ni with Co is limited by the relatively high price of Co and there have been efforts to replace some parts of Ni with cheaper metals such as Mn and Fe. For instance, Hwang et al.

[20,21] reported that the substitution of less than 30 at.% of Ni with Mn ( $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ ,  $y \leq 0.3$ ) gave improved electrochemical properties [20,21]. Other research has shown improvement in the electrochemical properties of Ni-based cathode materials by coating metal oxides such as  $\text{ZrO}_2$  and  $\text{Al}_2\text{O}_3$  on the surface of particles [22–26].

The electrochemical properties of lithiated mixed transition metal oxides are also influenced by structural properties such as hexagonal ordering, degree of cation mixing, and crystallinity, as well as by chemical composition.

In order to allow use as a cathode material and to guarantee high electric charging capacity, physical properties such as morphology and tap-density also have to be controlled precisely during the synthesis. In general, high tap-density particles can be obtained by increasing the crystallinity and grain size of crystals, but this leads to loss of specific charging capacity. Therefore, there is a limit to increasing tap-density by crystallinity and grain size. Another way to increase tap-density without loss of charging capacity is to fabricate uniform-sized spherical particles, as they can be packed more closely during the coating process of the cathode electrode due to good fluidity. The spherical nature of the particles provides advantages for producing a uniform, stable and dense coating of metal oxides as compared with particles that have an irregular morphology.

As noted earlier, there have been numerous efforts to prepare uniform spherical and high tap-density cathode materials without increasing the crystallinity or the grain size of crystals for high specific charging capacity. Preparation methods for

\* Corresponding author. Tel.: +82 42 860 7672; fax: +82 42 860 7590.  
E-mail address: [ykpark@kriect.re.kr](mailto:ykpark@kriect.re.kr) (Y.-K. Park).

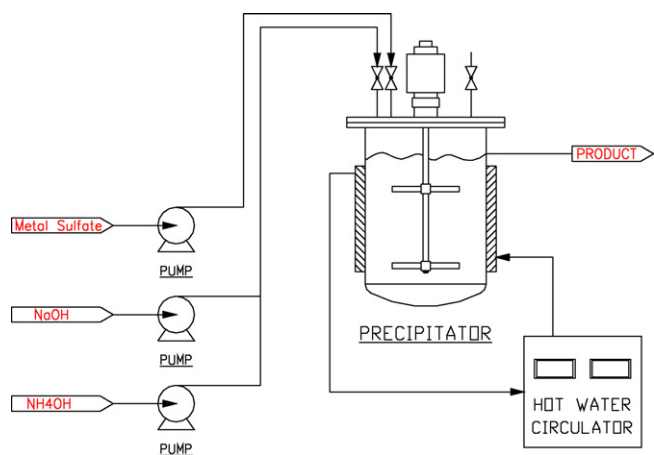


Fig. 1. Experimental apparatus for continuous co-precipitation of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursor.

micro-sized spherical powder by controlled crystallization are well described for single and binary oxide systems such as  $\text{LiCoO}_2$  [27] and  $\text{LiNi}_{0.80}\text{Co}_{0.20}\text{O}_2$  [28–34]. Also, many studies have applied co-precipitation methods for the production of a ternary oxide system of Ni, Co, and Mn [35–39]. However, because all of the aforementioned approaches involve preparation in a batch reactor, it is difficult to assess the effect of the synthesis conditions on the morphology and physical and chemical properties. Therefore, in the present work, systematic studies for the preparation of a ternary oxide of Ni, Co, and Mn under continuous precipitation conditions are conducted.

Considering preparation cost, improved tap-density and electrochemical properties brought by Mn to a  $\text{LiNiCoO}_2$  cathode material, a uniform spherical  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powder is prepared by a continuous co-precipitation method in aqueous phase using a continuous stirred tank reactor (CSTR). The effect

of preparation conditions, such as pH,  $\text{NH}_4\text{OH}$  concentration and co-precipitation time, are investigated and an attempt is made to correlate these conditions with physical and chemical properties. Finally, specific charging capacity tests and a retention analysis are carried out on the prepared  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ .

## 2. Experimental

### 2.1. Preparation of $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$ precursor

Details of the co-precipitation apparatus are shown in Fig. 1. The continuous co-precipitation of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  was carried out in a specially designed water-jacketed CSTR of 1000 ml capacity. Initially, the reactor was filled to 80 vol.% with distilled water and the pH of the water was then adjusted with 40 ml of 29 wt.%  $\text{NH}_4\text{OH}$  and a few drops of 25 wt.%  $\text{NaOH}$  solution. The solution was stirred at 500 rpm while maintaining the temperature at  $45^\circ\text{C}$  by circulating hot water through a jacket that enclosed the reactor. 1.5 M aqueous solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  corresponding to a molar composition of 0.80, 0.15 and 0.05, respectively, was introduced continuously into the reactor by a peristaltic pump and the product that overflowed out of the reactor was collected periodically. To induce co-precipitation of metal hydroxides, 25 wt.%  $\text{NaOH}$  solution was fed into the reactor by another peristaltic pump and the feeding rate was adjusted for desired pH. As a complexing agent, 29 wt.%  $\text{NH}_4\text{OH}$  solution was introduced and the flow rate was regulated by a mass flow controller to maintain the desired  $\text{NH}_3$ :metal molar ratio. The total feed flow rate was adjusted to maintain an average residence time of 10 h. The product that overflowed out of the reactor was collected periodically for analysis. The precipitation was carried out continuously until both the particle size and morphology reached a steady state. The collected products were neutralized by washing with distilled water and then drying at  $110^\circ\text{C}$  with hot air for 12 h.

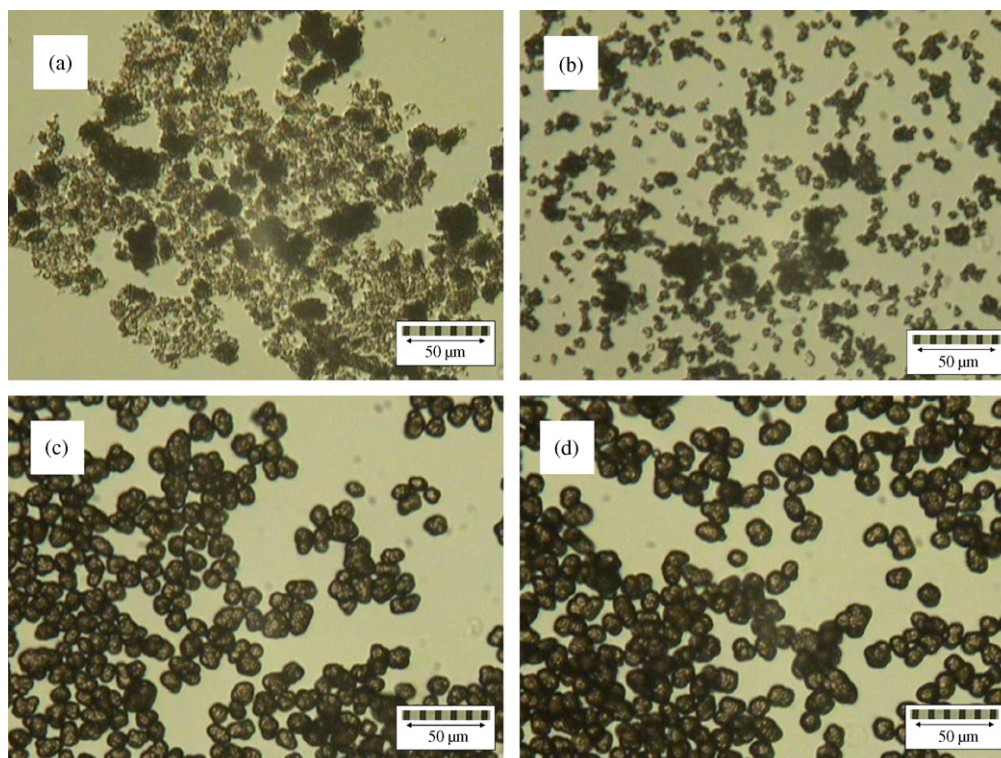
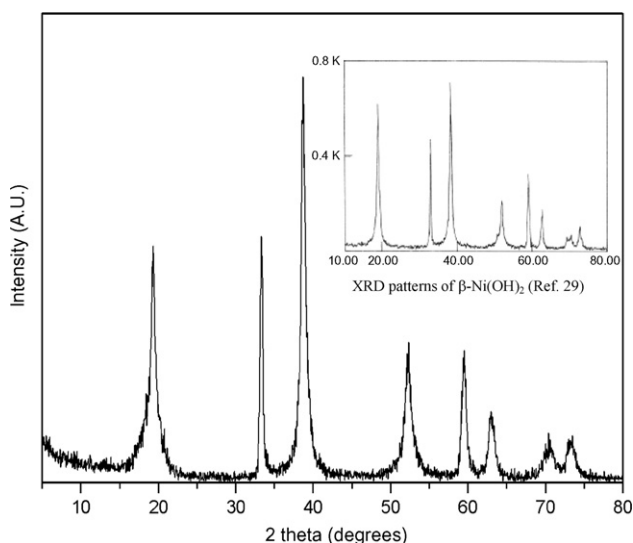


Fig. 2. Optical microscope images of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  depending on precipitation time: (a) 1 h, (b) 8 h, (c) 24 h and (d) 32 h.



**Fig. 3.** XRD pattern of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles obtained after 32 h co-precipitation (same sample shown in Fig. 2(d)).

## 2.2. Preparation of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$

The  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles, prepared by the co-precipitation method, were mixed thoroughly with a 2 at.% excess of a stoichiometric amount of  $\text{LiOH}\cdot\text{H}_2\text{O}$  (molar ratio of 1.02) to compensate for the calcining loss. The particles were then calcined in a muffle furnace for 12 h under air atmosphere at 650, 700, 750, 800, 850 and 900 °C, respectively.

## 2.3. Characterization

SEM images were taken and a composition analysis was conducted using a Philips XL30S FEG scanning electron microscope equipped with an EDAX Phoenix energy dispersive X-Ray spectrometer. The XRD patterns were acquired by means of a Rigaku D/MAX-2200 V X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation. To measure the cation-mixing effect, the  $I(003)/I(104)$  ratio and  $R$  values were calculated from the XRD patterns.

An ICP analysis was carried out using a Jobin Yvon Ultima-C inductively coupled plasma-atomic emission spectrometer. The tap-density of the powders was measured by the following procedure. The known weight of powder was placed in a 10 ml measuring cylinder (0.1 ml resolution) and tapped on a laboratory table until a constant volume was obtained. The weight of the sample was then divided by the volume to obtain the tap-

**Table 2**

Tap-density of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  depending on pH and  $\text{NH}_3$ :metal molar ratio.

Sample name	$\text{NH}_3$ :metal molar ratio	pH	Tap-density ( $\text{g cm}^{-3}$ )
<i>Effect of pH</i>			
CMP-1	1.0	9.5–10.0	1.46
CMP-2	1.0	10.8–10.9	1.58
CMP-3	1.0	11.2–11.3	1.66
CMP-4	1.0	11.3–11.4	1.76
CMP-5	1.0	11.5–11.6	2.00
CMP-6	1.0	11.7–11.8	1.76
CMP-7	1.0	11.9–12.0	1.66
<i>Effect of <math>\text{NH}_3</math>:metal molar ratio</i>			
CMP-8	1.2	11.5–11.6	1.50
CMP-5	1.0	11.5–11.6	2.00
CMP-9	0.8	11.5–11.6	1.58
CMP-10	0.6	11.5–11.6	1.50

density in  $\text{g ml}^{-1}$ . For measurement of the charging capacity, a coin-type half-cell was made with cathode materials consisting of 90 wt.%  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ , 5 wt.% carbon black, and 5 wt.% PVDF in NMP, a polyethylene separator, an electrolyte solution of 1 M  $\text{LiPF}_6$  in ethyl carbonate/dimethyl carbonate (1:1 vol.%), and a lithium metal anode. The charge–discharge profiles of the coin cell were obtained in a potential range of 4.3–3.0 V and at a current rate of 0.1, 0.2, 0.5 and 1 C. For measurement of the capacity retention, the cell was cycled between 4.3 and 3.0 V at 0.1, 0.2 and 0.5 C, respectively, and then 40 times at 1.0 C.

## 3. Results and discussion

### 3.1. Characteristics of $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$ precursor

Co-precipitation of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  was carried out continuously in a water-jacketted CSTR reactor (Fig. 1) and the morphology change of the products was monitored periodically by an optical microscope. At the beginning of the reaction, primarily fine particles are formed and then combine with each other to form irregular-shaped and micron-sized agglomerates (Fig. 2(a) and (b)). The particles grow gradually and develop a smooth and uniform spherical morphology without further agglomeration. After 24 h of precipitation, a steady state is reached, at which the particle size ranges from 10 to 15  $\mu\text{m}$  (Fig. 2(c) and (d)). Finally, the particles obtained after 32 h of precipitation have a spherical shape and show a quite narrow size-distribution.

During co-precipitation,  $\text{NH}_3$  and  $\text{NaOH}$  are involved in the reaction according to the following schemes, respectively, and the

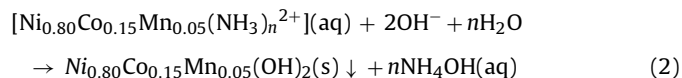
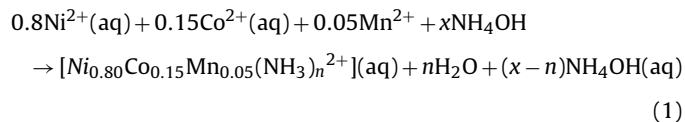
**Table 1**

Composition of prepared  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursor analyzed by ICP.

Sample name	$\text{NH}_3$ :metal molar ratio	pH	$\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$ precursor <sup>a</sup> composition (at.%)		
			Ni	Co	Mn
<i>Effect of pH</i>					
CMP-1	1.0	9.5–10.0	77.4	17.0	5.6
CMP-3	1.0	11.2–11.3	78.7	16.0	5.2
CMP-5	1.0	11.5–11.6	79.0	16.1	4.8
CMP-6	1.0	11.7–11.8	78.7	16.0	5.3
CMP-7	1.0	11.9–12.0	79.6	15.5	4.9
<i>Effect of <math>\text{NH}_3</math>:metal molar ratio</i>					
CMP-5	1.0	11.5–11.6	79.0	16.1	4.8
CMP-9	0.8	11.5–11.6	79.1	15.8	5.0
CMP-10	0.6	11.5–11.6	79.6	15.4	5.0

<sup>a</sup> Atomic composition of metal salt solution used for preparation of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursor = 80.0 at.% Ni:15.0 at.% Co:5.0 at.% Mn.

morphology and size of the primary particles are determined by their reaction rate.



To confirm the structure and chemical composition of the prepared  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles, XRD and ICP analyses were carried out for the samples described in Fig. 2(d). As shown in Fig. 3, the obtained  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles give similar

XRD patterns to that of  $\beta\text{-Ni}(\text{OH})_2$  [29]. The ICP analysis also reveals that the metal composition of the obtained  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles is similar to that of the starting metal salt solution, with the difference in composition being less than 1.0 at.% at the optimum pH and  $\text{NH}_3$ :metal molar ratio (Table 1). From the SEM, XRD and ICP data, it can be concluded that mono-dispersed, spherical  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  having ternary metal components can be synthesized successfully by the continuous co-precipitation method. Another important finding is that the chemical composition of the precipitates can be controlled precisely by simply manipulating the composition of the starting metal salt solution.

The morphology and tap-density of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles is strongly influenced by the pH and  $\text{NH}_3$ :metal molar

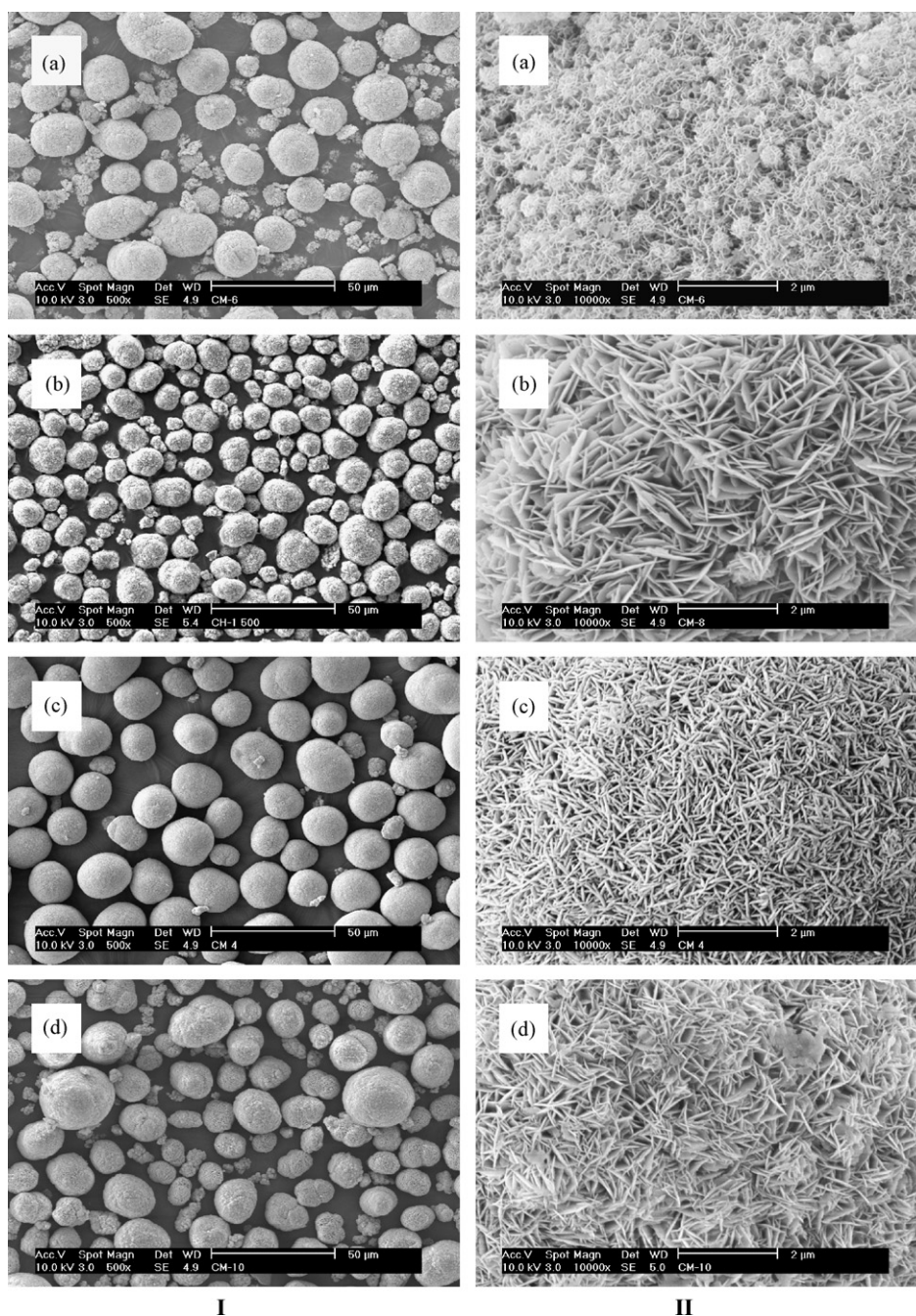


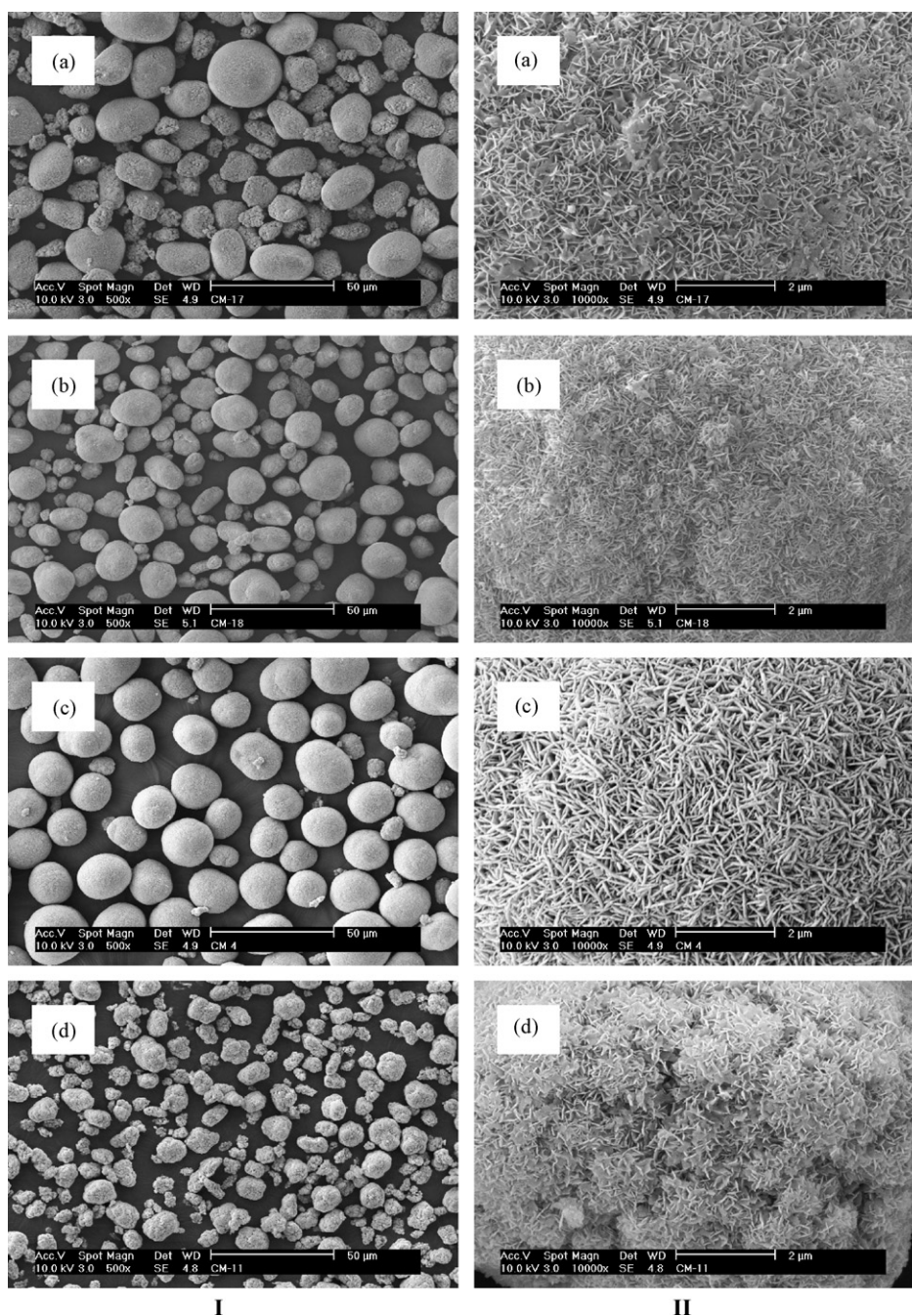
Fig. 4. SEM images of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  powders obtained at  $\text{NH}_3$ :metal molar ratio of 1.0 after 24 h precipitation at different pH ranges: (a) 9.5–10.0, (b) 11.2–11.3, (c) 11.5–11.6 and (d) 11.9–12.0 (magnification: I=500 $\times$  and II=10,000 $\times$ ).

ratio. There exists an optimum pH and  $\text{NH}_3$ :metal molar ratio for a high tap-density (Table 2). The tap-density increases gradually and shows a maximum value of 2 at a pH range of 11.5–11.6, and then decreases as the pH is increased further. The  $\text{NH}_3$ :metal molar ratio also influences the tap-density and the highest value is obtained at a  $\text{NH}_3$ :metal molar ratio of 1.0.

The macro- and microstructures of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles are also strongly influenced by the precipitation conditions. SEM images of the spherical  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles collected at different pH values and  $\text{NH}_3$ :metal molar ratios are presented in Figs. 4 and 5. Depending on the precipitation conditions, the obtained precipitates reveal quite broad particle size and shape distributions. The precipitates obtained at optimum pH and  $\text{NH}_3$ :metal molar ratio give dense and spherical-shaped

particles with a narrow size-distribution (Figs. 4-I(c) and 5-I(c)). When the pH and  $\text{NH}_3$ :metal molar ratio are not adjusted properly, however, irregular-shaped porous particles are obtained. Furthermore, different microstructures are obtained depending on the pH and  $\text{NH}_3$ :metal molar ratio. As can be seen in the SEM images (Figs. 4-II and 5-II), the particles consist of agglomerated needle-like microcrystalline grains. The particles obtained at optimum pH and  $\text{NH}_3$ :metal molar ratio have a closely packed microstructure (Figs. 4-II(c) and 5-II(c)), whereas the particles obtained at different precipitation conditions are not as smooth as those produced under optimum conditions.

The morphology, microstructure and tap-density of the particles correlate well with the synthesis parameters of pH and  $\text{NH}_3$ :metal molar ratio. Taking these results into consideration, a  $\text{NH}_3$ :metal



**Fig. 5.** SEM images of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  powders obtained at pH range 11.5–11.6 and different  $\text{NH}_3$ :metal molar ratios: (a) 0.6, (b) 0.8, (c) 1.0, and (d) 1.2 (magnification: I = 500 $\times$  and II = 10,000 $\times$ ).

**Table 3**  
Tap-density,  $I(003)/I(104)$  ratio and  $R$  values depending on calcination temperature.

Name of the $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ samples	Metal hydroxide precursor	Calcination temperature ( $^{\circ}\text{C}$ )	Tap-density ( $\text{g cm}^{-3}$ )	$I(003)/I(104)^a$ value	$R$ value <sup>a</sup>
<i>Effect of calcination temperature</i>					
LCMP-3	CMP-3	650		1.11	0.79
LCMP-3	CMP-3	700		1.25	0.66
LCMP-3	CMP-3	750		1.47	0.52
LCMP-3	CMP-3	800		1.41	0.52
LCMP-3	CMP-3	850		1.08	0.62
LCMP-3	CMP-3	900		1.09	0.60
<i>Effect of pH</i>					
LCMP-1	CMP-1	750	1.76	1.43	0.58
LCMP-3	CMP-3	750	1.87	1.47	0.52
LCMP-5	CMP-5	750	2.72	1.30	0.44
LCMP-7	CMP-7	750	2.14	1.40	0.48
<i>Effect of <math>\text{NH}_3</math>:metal molar ratio</i>					
LCMP-8	CMP-8	750		1.46	0.58
LCMP-5	CMP-5	750	2.72	1.30	0.44
LCMP-9	CMP-9	750		1.44	0.56
LCMP-10	CMP-10	750		1.35	0.59

<sup>a</sup>  $I(003)/I(104)$  ratio and  $R$  values were calculated from XRD patterns.

molar ratio of 1 and a pH range of 11.5–11.6 are deemed to be the most ideal conditions for the formation of spherical-shaped and higher-density  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles by the continuous co-precipitation method.

### 3.2. Characterization of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$

To obtain a final cathode material of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ ,  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursors were lithiated with  $\text{LiOH}\cdot\text{H}_2\text{O}$  and then calcined at different temperatures. The nomenclature of the lithiated powders, tap-density,  $I(003)/I(104)$  ratio, and  $R$  values of samples prepared under different calcination temperatures, pH, and  $\text{NH}_3$ :metal molar ratio are presented in Table 3.

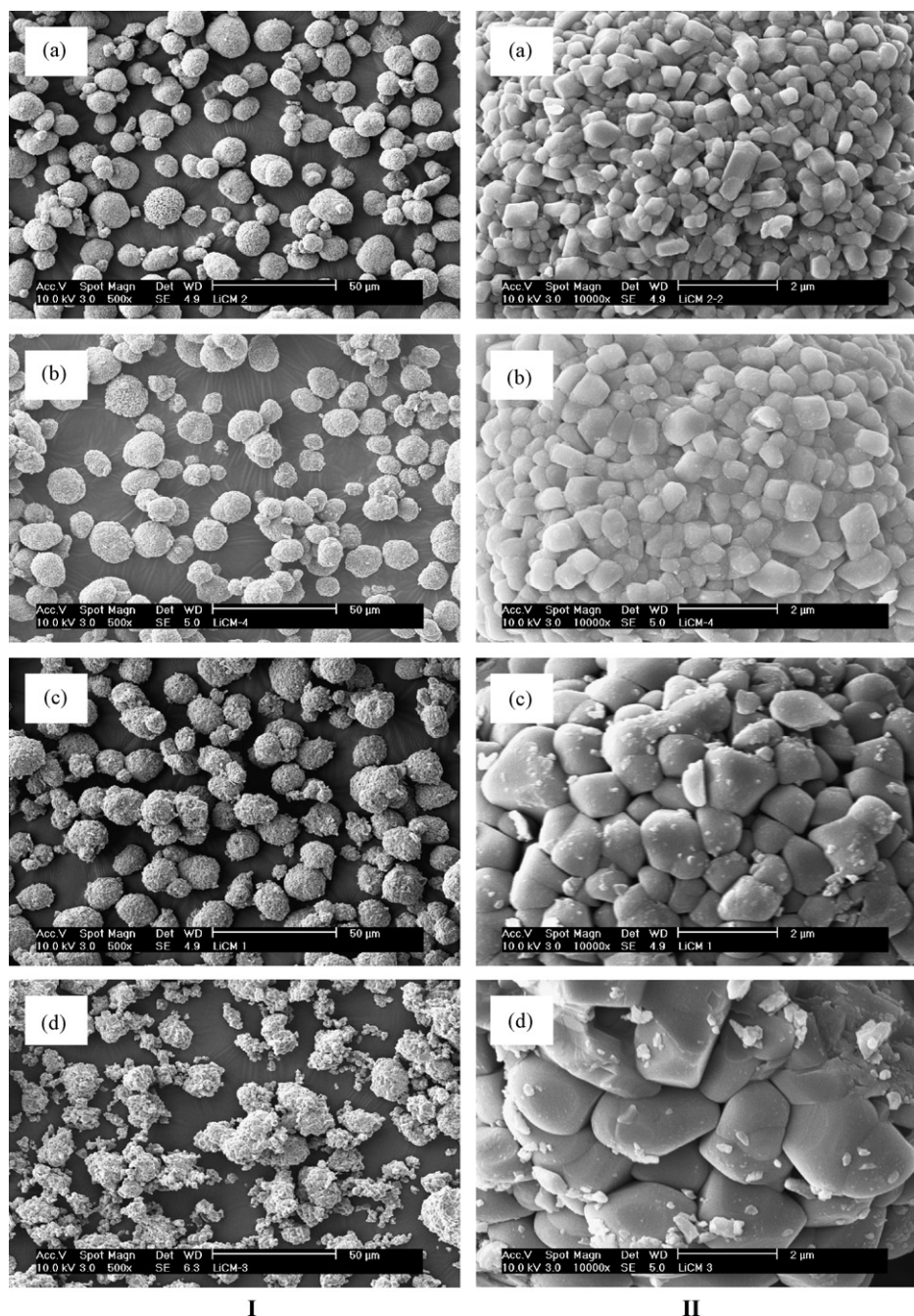
To decide the optimum calcination temperature, a  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursor (CMP-3) prepared in a continuous co-precipitator was lithiated and then calcined at different temperatures from 650 to 900  $^{\circ}\text{C}$  (Table 3). As shown in Fig. 6, the particles are comprised of closely packed, cube-like, crystalline grains which are considerably different from the fine, needle-like, crystalline grains of the  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursor (Fig. 4(b)). The grain size of the particles increases as the calcination temperature is increased and this indicates that the grains merge together and become larger at higher calcination temperatures. The spherical morphology of the initial particles is maintained up to the calcination temperature of 800  $^{\circ}\text{C}$ , but the particles collapse and become irregular shaped when the calcination temperature is raised beyond 850  $^{\circ}\text{C}$ . Therefore, to maintain their initial morphology and small grain size, the lithiated precursors should be calcined at temperatures below 800  $^{\circ}\text{C}$ .

The XRD patterns of the  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powders calcined at different temperatures are presented in Fig. 7. The patterns are characteristic of a hexagonal  $\alpha$ - $\text{NaFeO}_2$  structure of space group  $R3-m$  [30] without any other impurity phases. The samples calcined at 650 and 700  $^{\circ}\text{C}$  are less crystalline than those calcined at higher temperatures. The ratio of the intensities of the (003) and (104) peaks,  $I(003)/I(104)$ , is an important parameter to predict the electrochemical properties of cathode materials. A  $I(003)/I(104)$  value lower than 1.1 is an indication of a high degree of cation mixing, revealing the presence of transition metal ions in the lithium sites (3b sites) [20,31–33]. These transition metals, which are present in 3b sites, act as pinning sites for transition metal layers and reduce the lithium diffusion coefficient and power capability of the cathode. The  $R$  value, defined as the ratio of the intensities of doublet peaks (006) and (102) to the (101) peak, is an indicator of the extent of hexagonal ordering

[11]. The lower the  $R$  value, the better is the hexagonal ordering [11,34]. The  $I(003)/I(104)$  ratios presented in Table 3 show that the samples calcined at temperatures above 800  $^{\circ}\text{C}$  exhibit a higher degree of cation mixing. Also, the samples calcined at 650, 700, 850 and 900  $^{\circ}\text{C}$  exhibit poor hexagonal ordering compared with those calcined at 750 and 800  $^{\circ}\text{C}$ . These observations reveal that the optimum temperature range is 750–800  $^{\circ}\text{C}$  for the calcination of a  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  and  $\text{LiOH}$  mixture to obtain an oxide without cation mixing and with the highest hexagonal ordering. In this temperature range, however, the crystallite size of the particles is smaller at 750  $^{\circ}\text{C}$  (Fig. 6). Therefore, a calcination temperature of 750  $^{\circ}\text{C}$  was chosen as the optimum temperature, because an increase of crystallite size may reduce the charging capacity of the material.

In order to assess the effect of pH and  $\text{NH}_3$ :metal molar ratio during the preparation of the precursor on the properties of the final  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ ,  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  powders prepared under different pH and  $\text{NH}_3$ :metal molar ratios were subjected to Li addition and then calcined at 750  $^{\circ}\text{C}$  (Figs. 8 and 9). As expected, all samples have similar XRD patterns, regardless of the preparation conditions concerning pH and  $\text{NH}_3$ :metal molar ratio. The XRD patterns are not strongly influenced by the preparation conditions compared with the morphology and tap-density.

In addition, all samples lithiated at 750  $^{\circ}\text{C}$  have an  $I(003)/I(104)$  ratio higher than 1.1 without cation mixing (Table 3). By contrast, the  $R$  values of the  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  samples are found to vary significantly with respect to the preparation conditions of their hydroxide precursors, such as pH and  $\text{NH}_3$ :metal molar ratio. After fixing the  $\text{NH}_3$ :metal molar ratio at 1.0, the pH was changed from 9.5 to 12.0. The  $R$  value decreases as the pH is increased and reaches a minimum value of 0.44 at a pH range of 11.5–11.6, which is the optimum condition in terms of the preparation of powders with the highest tap-density. Similarly, after fixing the pH range at 11.5–11.6, the  $\text{NH}_3$ :metal molar ratio was changed from 0.6 to 1.2. As the  $\text{NH}_3$ :metal molar ratio is increased from 0.6 to 1.0, the  $R$  value decreases from 0.59 to 0.44. Further increase in the  $\text{NH}_3$ :metal molar ratio to 1.2 leads to an increase in the  $R$  value to 0.58. These observations demonstrate that the preparation conditions of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$ , such as pH and  $\text{NH}_3$ :metal ratio, are important synthesis parameters and are closely related with the properties of the final  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ , such as hexagonal ordering, cation mixing and, consequently, the electrochemical properties. Therefore, the synthetic conditions of the precursor should be optimized for hexagonal ordering and minimization of cation mixing.



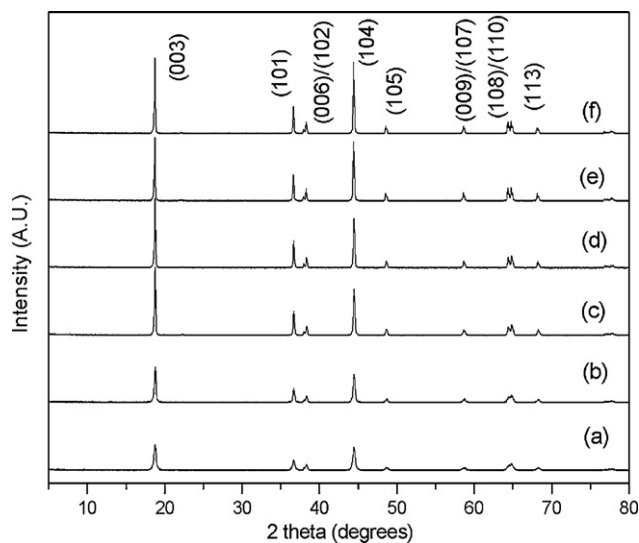
**Fig. 6.** SEM images of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  (LCMP-3) after calcining at different temperatures: (a) 750 °C, (b) 800 °C, (c) 850 °C and (d) 900 °C (magnification: I = 500× and II = 10,000×).

The tap-density of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powder is directly related to that of their hydroxide precursors (Table 3). The higher the tap-density of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  powder, the higher is the obtained tap-density of  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powder.

### 3.3. Specific capacity of $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$

In order to evaluate its cathodic properties, LCMP-5(750), which has the highest tap-density, no appreciable cation mixing and the lowest  $R$  value, was subjected to specific capacity measurement by fabricating a coin-type cell. The first cycle charge and discharge curves at a 0.1, 0.2, 0.5 and 1.0C rate are given in Fig. 10. The charge–discharge capacities at 0.1, 0.2, 0.5 and 1.0C rates are found to be 222 (200), 201 (194), 194 (184) and 184

(176)  $\text{mAh g}^{-1}$ , respectively, where the values in parentheses indicate discharge capacity. In order to investigate its capacity retention capability, LCMP-5(750) was subjected to one cycle at the 0.1, 0.2 and 0.5C rates, respectively, and then to 40 cycles at the 1.0C rate (Fig. 11). As can be seen in the specific discharge capacity curve, even at the 1.0C rate LCMP-5(750) exhibits good capacity retention. After 40 cycles, the specific capacity of LCMP-5(750) is  $161 \text{ mAh g}^{-1}$ , which corresponds to 8.6% fading of the initial capacity. This notable performance of the spherical  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  might be due to the homogeneous distribution of transition metal ions, which originates from the preparation procedure applied to the  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  precursor in order to maintain its layered structure. That is, the mixing of the three metal salt solutions before continuous co-

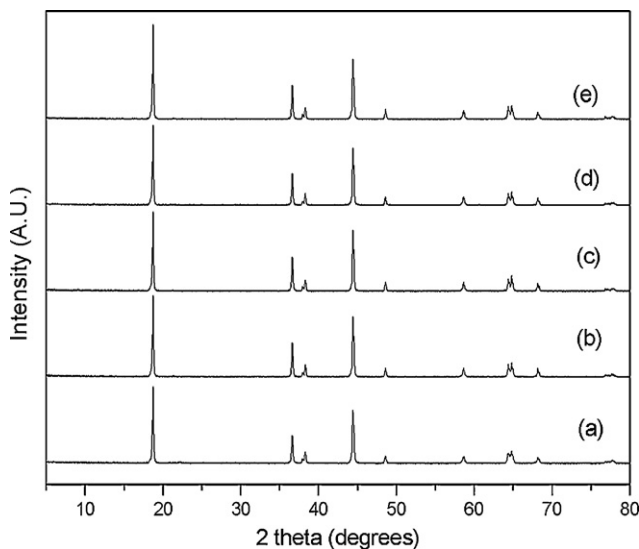


**Fig. 7.** XRD patterns of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  (LCMP-3) after calcining at different temperatures: (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 800 °C, (e) 850 °C and (f) 900 °C.

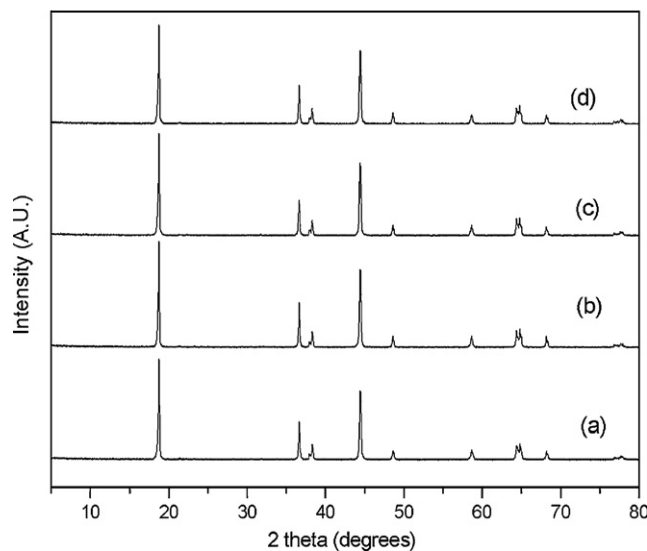
precipitation results in a good atomic level distribution of transition metal ions in the prepared precursor of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$ . In addition, the layered structure of  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  allows for ready formation of a well-ordered, layered structure in  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$ . The initial discharge capacity and capacity retention of the spherical  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  prepared in the continuous co-precipitator are better than the previous results of  $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$  materials prepared by other preparation methods [20,21,35–37]. Therefore, the production of spherical  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powder by this continuous co-precipitation method is a promising route to produce a cathode material for Li-ion batteries.

#### 4. Conclusions

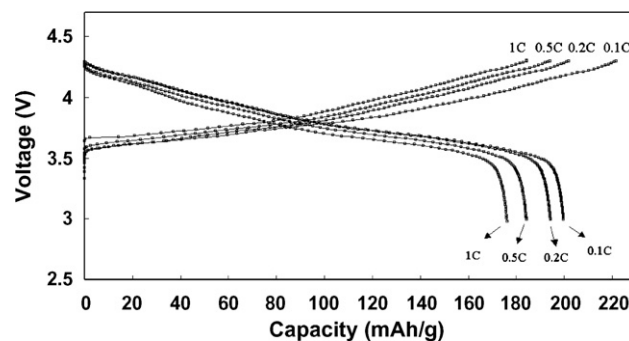
The preparation conditions of pH and  $\text{NH}_3$ :metal molar ratio in continuous co-precipitation have significant effects on the particle morphology, tap-density and structural properties of



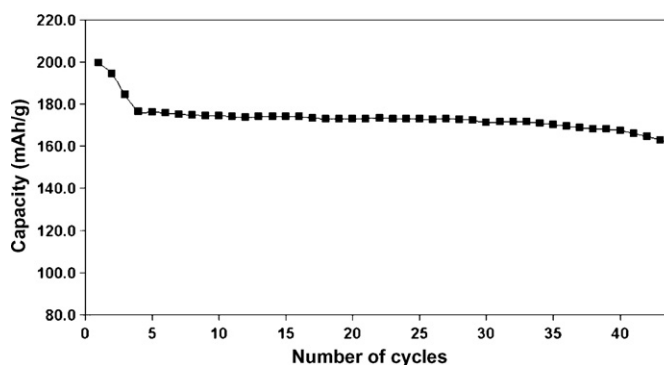
**Fig. 8.** XRD patterns of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  prepared at different pH ranges with a  $\text{NH}_3$ :metal molar ratio of 1 after calcining at 750 °C: (a) 9.5–10, (b) 11.2–11.3, (c) 11.5–11.6, (d) 11.7–11.8 and (e) 11.9–12.0.



**Fig. 9.** XRD patterns of  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  prepared at different  $\text{NH}_3$ :metal molar ratios in pH range 11.5–11.6: (a) 1.2, (b) 1.0, (c) 0.8 and (d) 0.6.



**Fig. 10.** Charge–discharge characteristic of LCMP-5(750) at 0.1, 0.2, 0.5 and 1.0 C.



**Fig. 11.** Specific charging capacity of LCMP(750) as a function of cycle number. Coin half-cell cycled between 4.3 and 3.0 V at 0.1, 0.2 and 0.5 C, then for 40 cycles at 1.0 C.

$\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powders. A  $\text{NH}_3$ :metal molar ratio of 1.0 and a pH range of 11.5–11.6 are found to be the optimum conditions for obtaining smooth and spherical  $\text{Ni}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}(\text{OH})_2$  particles that have the highest tap-density. The spherical  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  particles have a hexagonally ordered, layered structure, and the degree of their hexagonal ordering and the extent of cation mixing depend on the calcination temperature and preparation conditions, such as pH and  $\text{NH}_3$ :metal molar ratio. Given the high initial charging capacity and more than 91% capacity retention after 40 charge–discharge cycles at a 1.0 C rate together with the spherical nature and high tap-density, it is con-



cluded that the spherical  $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Mn}_{0.05}\text{O}_2$  powders prepared by this continuous co-precipitation method are promising cathode materials for Li-ion batteries.

### Acknowledgment

The author K.K.C. gratefully acknowledges the Korea Science and Engineering Foundation for a post-doctoral fellowship under the 2004 KOSEF Post-doctoral Fellowship Program for Foreign Researchers.

### References

- [1] J.R. Dahn, E.W. Fuller, M. Obrava, U. von Sacken, *Solid State Ionics* 69 (1994) 265.
- [2] T. Ohzuku, A. Ueda, *Solid State Ionics* 69 (1994) 201.
- [3] M.N. Obrovac, O. Mao, J.R. Dahn, *Solid State Ionics* 112 (1998) 9.
- [4] J. Maruta, H. Yasuda, M. Yamachi, *J. Power Sources* 90 (2000) 89.
- [5] S.H. Park, K.S. Park, Y.K. Sun, K.S. Nahm, Y.S. Lee, M. Yoshio, *Electrochim. Acta* 46 (2001) 1215.
- [6] A. Rougier, I. Saadoune, P. Gravereau, P. Willmann, C. Delmas, *Solid State Ionics* 90 (1996) 83.
- [7] A. Hirona, R. Kanno, Y. Kawamoto, Y. Nitta, K. Okamura, T. Izumi, F. Izumi, *J. Solid State Chem.* 134 (1997) 1.
- [8] Q. Zhong, U. von Sacken, *J. Power Sources* 54 (1995) 221.
- [9] J. Kim, K. Amine, *J. Power Sources* 104 (2002) 33.
- [10] C. Pouillier, L. Croguennec, P. Biensan, P. Willmann, C. Delmas, *J. Electrochem. Soc.* 147 (2000) 2061.
- [11] J.N. Reimers, E. Rossen, C.D. Jones, J.R. Dahn, *Solid State Ionics* 61 (1993) 335.
- [12] J. Cho, *Chem. Mater.* 12 (2000) 3089.
- [13] B.V.R. Chowdari, G.V.S. Rao, S.Y. Chow, *Solid State Ionics* 140 (2001) 55.
- [14] P. Kalyani, N. Kalaiselvi, N.G. Renganathan, M. Raghavan, *Mater. Res. Bull.* 39 (2004) 41.
- [15] H. Cao, B. Xia, N. Xu, C. Zhang, *J. Alloys Compd.* 376 (2004) 282.
- [16] C. Delmas, I. Saadoune, A. Rougier, *J. Power Sources* 44 (1993) 595.
- [17] D. Caurant, N. Baffier, B. Cacia, J.P. Pereira-Ramos, *Solid State Ionics* 91 (1996) 45.
- [18] W. Li, J.C. Currie, *J. Electrochem. Soc.* 144 (1997) 2773.
- [19] J. Cho, H.S. Jung, Y.C. Park, G.B. Kim, H.S. Lim, *J. Electrochem. Soc.* 147 (2000) 15.
- [20] B.J. Hwang, Y.W. Tsai, C.H. Chen, R. Santhanam, *J. Mater. Chem.* 13 (2003) 1962.
- [21] Z. Liu, A. Yu, J.-Y. Lee, *J. Power Sources* 81 (1999) 416.
- [22] M. Mladenov, R. Stoyanova, E. Zhecheva, S. Vassilev, *Electrochem. Commun.* 3 (2001) 410.
- [23] H.-J. Kweon, S.J. Kim, D.G. Park, *J. Power Sources* 88 (2000) 255.
- [24] J. Cho, Y.-W. Kim, B. Kim, J.-G. Lee, B. Park, *Angew. Chem.* 115 (2003) 1656.
- [25] A. Choblet, H.C. Shiao, H.-P. Lin, M. Salomon, V. Manivannan, *Electrochem. Solid State Lett.* 4 (2001) A65.
- [26] Z. Wang, C. Wu, L. Liu, F. Wu, L. Chen, X. Huang, *J. Electrochem. Soc.* 149 (2002) A466.
- [27] J. Ying, C. Wan, C. Jiang, Y. Li, *J. Power Sources* 129 (2004) 264.
- [28] J. Ying, C. Wan, C. Jiang, Y. Li, *J. Power Sources* 99 (2001) 78.
- [29] C. Zhaorong, L. Gongan, Z. Yujuan, C. Jianguo, D. Yunchang, *J. Power Sources* 252 (1998) 74.
- [30] W. Li, J.N. Reimers, J.R. Dahn, *Solid State Ionics* 67 (1993) 123.
- [31] J. Kim, P. Fulmer, A. Manthiram, *Mater. Res. Bull.* 34 (1999) 571.
- [32] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, *Electrochim. Acta* 38 (1993) 1159.
- [33] Y. Cao, M.V. Yakovleva, W.B. Ebner, *Electrochem. Solid State Lett.* 1 (1998) 117.
- [34] G.T.-K. Fey, J.-G. Chen, Z.-F. Wang, H.-Z. Yang, T.P. Kumar, *Mater. Chem. Phys.* 87 (2004) 246.
- [35] Y. Chen, G.X. Wang, K. Konstantinov, H.K. Liu, S.X. Dou, *J. Power Sources* 119 (2003) 184.
- [36] J.K. Ngala, N.A. Chernova, M. Ma, M. Mamak, P.Y. Zavalij, M.S. Whittingham, *J. Mater. Chem.* 14 (2004) 214.
- [37] M. Yoshio, H. Noguchi, J.-I. Itoh, M. Okada, T. Mouri, *J. Power Sources* 90 (2000) 176.
- [38] S. Jouanneau, J.R. Dahn, *Chem. Mater.* 15 (2003) 495.
- [39] A.D. Epifanio, F. Croce, F. Ronci, V.R. Albertini, E. Traversa, B. Scrosati, *Phys. Chem. Chem. Phys.* 3 (2001) 4399.