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# Synthesis of $Li_{1+x}[Ni_pCo_qMn_r]O_2$ as positive electrode for lithium-ion batteries by optimizing its synthesis conditions via carbonate co-precipitation method

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Spherical  $Li_{1+x}[Ni_{0.22}Co_{0.13}Mn_{0.65}]O_2$  cathode material for lithium-ion battery was synthesized by co-precipitation method. The mixture of prepared carbonate precursor and lithium carbonate was calcined at 950 °C for 24 hrs in air. The XRD patterns of all the prepared powders show hexagonal  $\alpha$ -NaFeO<sub>2</sub> structure (space group: R-3m, 166) and existence of  $Li_2MnO_3$  phase in the composite structure. The morphology of the prepared powders has spherical agglomerates with the particle size varying from 5~8 µm. The observed charge and discharge capacity for the first cycle is 298.5, 219 mAhg<sup>-1</sup> for  $Li_{1.44}Ni_{0.23}Co_{0.12}Mn_{0.65}O_2$ .

Keywords: Lithium secondary battery, Cathode, Co-precipitation.

## Introduction

Research on lithium secondary battery is being actively conducted as there is an increasing demand on batteries with high power and high energy density for the applications of HEV and EV. The active LiCoO<sub>2</sub> cathode material of lithium secondary batteries is used widely for IT application at present because it has an outstanding charge/discharge cycling performance and its mass production is simple as it can be easily synthesized [1]. Among the known intercalation materials for rechargeable lithium battery cathodes, LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiNi<sub>1/3</sub>Mn<sub>1/3</sub> Co<sub>1/3</sub> and their composite materials have been studied extensively [2]. Cathode material of HEV and PHEV have to satisfactory high capacity and low cost for developing Li ion battery. So, The complex layered compound of Li<sub>2</sub>MnO<sub>3</sub>-LiNi<sub>x</sub>CO<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> has also been investigated by many groups in recent years because of high capacity and good structural stability at high charged state high capacity and low cost [3-5].

These types of non-toxic cathode materials have the advantages of having structural stability under a wide operating voltage range from 2.5-5.0 V and high capacity [6-8]. A high percentage of the Manganese also reduces the overall material cost which will be commercially favorable of high electric vehicles (HEVs) [9]. Nevertheless, the long term cycling performances of this material is still not very satisfactory due to formation of LiMn<sub>2</sub>O<sub>4</sub> spinel compound [10]. However, We observed that higher lithium content can be put a stop to the formation of spinal phases.

Well-ordered hexagonal super lattice layered structure and semi-micro sized spherical particles are desirable for getting better electrochemical properties [1-6]. Selecting the synthesis method is critical to obtain the reported criteria [11]. So, co-precipitation method is permissible for a superior cationic distribution [12-13]. Therefore, the optimization of synthetic conditions of lithium and manganese excess cathode material is the basic requirement to prepare the efficient precursor. In this research work, co-precipitation method is used for preparing Li<sub>1+x</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub>/xLi<sub>2</sub>MnO<sub>3-(1-x)</sub>LiNi<sub>p</sub>Co<sub>q</sub> Mn<sub>r</sub>O<sub>2</sub> cathode material. The mixed transition metal carbonate was prepared using Na<sub>2</sub>CO<sub>3</sub> and NH<sub>4</sub>OH as chelating agent under N2 atmosphere. The spherical Li1+xNi0.22Co0.13 Mn<sub>0.65</sub>O<sub>2</sub>/<sub>x</sub>Li<sub>2</sub>MnO<sub>3</sub>-(1-x)LiNi<sub>p</sub>Co<sub>q</sub>Mn<sub>r</sub> O<sub>2</sub> was synthesized by mixing the precursor powder with Li<sub>2</sub>CO<sub>3</sub> followed by high temperature calcinations. The effect of the synthesis conditions on the physical properties of Li<sub>1+x</sub>  $Ni_{0.22}Co_{0.13}Mn_{0.65}O_2/xLi_2MnO_3-(1-x)LiNi_pCo_qMn_rO_2$  were investigated in detail.

#### **Experimental**

#### Synthesis of Li<sub>1+x</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> cathode materials

The precursor  $Ni_{0.22}Co_{0.13}Mn_{0.65}CO_3$  was synthesized by co-precipitation. An aqueous solution of NiSO<sub>4</sub>.6H<sub>2</sub>O, CoSO<sub>4</sub>.7H<sub>2</sub>O and MnSO<sub>4</sub>.H<sub>2</sub>O (cationic ratio of Ni + Co + Mn = 1) with a concentration of 1 M were pumped into a continuously stirred tank reactor (CSTR) under N<sub>2</sub> atmosphere. At the same time, Na<sub>2</sub>CO<sub>3</sub> (2 M) solution and the NH<sub>4</sub>OH solution were separately fed into the reactor.

The obtained Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>CO<sub>3</sub> precursor was thoroughly mixed with an appropriate amount of Li<sub>2</sub>CO<sub>3</sub> and calcined 950 °C for 24 hrs in air. X-ray diffraction patterns for the cathodes were obtained using a Siemens D-5000 diffractometer in the 20 range from 10 to 70 ° with Cu K $\alpha$  radiation ( $\lambda = 1.54068$ Å). The morphology of the obtained powder was observed with scanning electron microscope (SEM).

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To prepare the positive electrode, 80%  $Li_{1+x}Ni_{0.22}Co_{0.13}$ Mn<sub>0.65</sub>O<sub>2</sub> powder 10% super-P carbon black (Aldrich), N-methyl-2-pyrrolidone, and 10% PVdF (Kureha KF100) binder were added in a crucible. After two hours of grinding, the viscous slurry was coated on aluminum foil using a doctor blade to make a film with a uniform thickness. The film was then dried at 60 °C for 6 hrs and 120 °C for 6 hrs in a vacuum oven. The thickness of the cathode film was approximately 40 µm. The CR2016 type coin cell was assembled in a glove box using the above cathode film, lithium, a porous polyethylene film, and a  $1 \text{ M LiPF}_6$  solution in a 1:2 volume ratio of ethylene carbonate (EC)/dimethyl carbonate (DMC). The lithium metal foil was used as both the counter and reference electrode. After the coin cell assembly, the test cells were charged and discharged galvano-statically between 2.0 and 4.6 V versus Li/Li+, at a constant current density (170 mAg<sup>-1</sup> was assumed to be 1C rate). The cyclic voltammetry (CV) curves were obtained at 0.1 mVS<sup>-1</sup> and between 2.0-4.6 V. All the electrochemical measurements were carried out at 25 °C

## **Results and Discussion**

#### Cathode materials characterization

Co-precipitation of Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>CO<sub>3</sub> was carried out continuously in a CSTR reactor and the morphology change of the products was monitored periodically by an optical microscope. At the beginning of the reaction, fine particles are formed and then combine with each other to form irregular-shaped and micro-sized (Fig. 1(a-b)). The particles grow gradually and develop a smooth and uniform spherical morphology without further agglomeration. After the precipitation for 16 hrs, a steady state is reached, at which the particle size ranges  $5 \sim 15 \,\mu\text{m}$  (Fig. 1(c-d)). Finally, the particles obtained after 20 hrs of precipitation have a spherical



Fig. 1. Optical microscope images of  $Ni_{0.22}Co_{0.13}Mn_{0.65}CO_3$  depending on precipitation time: (a) 4, (b) 8, (c) 16 and (d) 32 hrs.

shape and show a quite narrow size-distribution.

The XRD patterns of LixNi<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> (x = 1.44, 1.6) are show in Fig. 2(a-b), respectively. The two-component characters of these structurally integrated materials are evident in the low-intensity ordering peaks at 2 $\theta$  of 21-25° (arrowed in Fig. 1(a-b)) that are characteristic of a Li<sub>2</sub>MnO<sub>3</sub>-type structure with LiMn<sub>6</sub> (or Ni substituted) cation arrangements in the transition metal layers. These ordering peaks are clearly visible in materials with a high Li<sub>2</sub>MnO<sub>3</sub> content and domain size, such as those selected for this investigation, but they become more difficult to detect by XRD for low Li<sub>2</sub>MnO<sub>3</sub> concentrations, particularly when cobalt is present [9].

The superior intensity are originated of  $Li_2MnO_3$ phases at higher value of x in  $Li_{1+x}[Ni_{0.22}Co_{0.13}Mn_{0.65}]$  $O_2$ . The hexagonal lattice parameter of various Li/M (M = Ni + Co + Mn) ratios are summarized in Table 1. The highest values of c/a and  $I_{003}/I_{104}$  are attained when the Li/M M = Ni + Co + Mn) mixing ratio is 1.44/1 which indicates comparatively a well-ordered hexagonal structure is formed in this ratio. Surface images (Fig. 3) provide the information about particle size. The average particle sizes of 1.44/1 and 1.6/1 Li/M (M = Ni + Co + Mn) ratio is almost same (5 ~ 8 µm). Conversely, the particle size is enlarged (5 ~ 8 µm) while the ratio between lithium and transition metal is higher than 1.44

The chemical composition of the prepared precursor and various lithium transition metal (Ni, Co, Mn) compounds was determined from ICP (Table 2). The expected Li/M ratio of was not maintained due to little amount of lithium loss at high calcined temperature [14] (950 °C).



Fig. 2. XRD patterns of the (a) x = 1.44, (b) x = 1.6 on x in the  $Li_xNi_{0.22}Co_{0.13}Mn_{0.65}O_2$ 

Table 1. Lattice parameters of  $Li_x Ni_{0.22} Co_{0.13} Mn_{0.65} O_2$  electrode materials.

LixNi0.22C00.13Mn0.65O2	a (sigma)	c (sigma)	c/a	$I_{003}/I_{104}$
X = 1.44	2.8546 (± 0.0002)	14.2466 (± 0.0008)	4.993	2.30
X = 1.6	2.855 (± 0.0001)	14.2590 (± 0.0009)	4.972	2.17



Fig. 3. SEM image of the (a) precursor, (b) x = 1.44, and (c) x = 1.6 on x in the  $Li_xNi_{0.22}Co_{0.13}Mn_{0.65}O_2$ .

#### **Electrochemical behavior**

The initial charge-discharge curves for the Li<sub>x</sub>Ni<sub>0.22</sub>  $Co_{0.13}Mn_{0.65}O_2$  (x = 1.44, 1.6) cell cycled between 2.0 and 4.6 V at a constant current density of 17 mAg<sup>-1</sup> are shown in Fig. 4. All the prepared samples have two distinguished voltage regions during the initial charge process. The voltage profiles of all samples start from the initial cell open circuit potential and monotonically increased to 4.45 V with a slope. After voltage reached at around 4.45 V, the voltage plateau was observed. The first voltage region below 4.45 V originated from the oxidation of the transition metal ions to tetravalent ion, while the voltage plateau region locating at 4.45 V is mainly due to electrochemical removal of Li<sub>2</sub>O [15-17]. It can be observed that the voltage profile of each sample varies with the composition change in particular x value (LixNi<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub>). As the amount of Li(x) increase, the charge voltage curve for the first voltage region (below 4.45 V) starts to shift to the higher voltage while the voltage plateau (at 4.45 V) became longer except for x = 1.6. The reason of decreased charge capacity at Li<sub>1.6</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> is attributed to the increasing oxidation state of metal ion and polarization of Li<sub>2</sub>MnO<sub>3</sub> component. The extent of initial charge reaction between 3.0 and 4.45 V, which is associated with lithium extraction from the  $LiMO_2$  (M = Ni, Co, Mn) component, decreases with increasing x, whereas the voltage plateau at  $4.45 \sim 4.6$  V, which is attributed



**Fig. 4.** 1<sup>st</sup> charge-discharge curves the (a) x = 1.44 and (b) x = 1.6 on x in the Li<sub>x</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub>/Li cell cycled in the voltage range of 2.0-4.6 V at a constant current density of 17 mA/g.

to the activation of the Li<sub>2</sub>MnO<sub>3</sub> component, lengthens with increasing x, expected except for Li<sub>1.6</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub> Mn<sub>0.65</sub>O<sub>2</sub> component. The high amount of Li<sub>2</sub>MnO<sub>3</sub> component delivered by the Li1.6Ni0.22Co0.13Mn0.65O2 electrode shown in Table 2, therefore, particularly noteworthy because it illustrate that a relatively small amount and high oxidation state of M (LiMO<sub>2</sub>), is not sufficient to a Li<sub>2</sub>MnO<sub>3</sub> electrode to electrochemical cycling when charged to high potential. The three integrated structure (LiMn<sub>2</sub>O<sub>4</sub>, Li<sub>2</sub>MnO<sub>3</sub>, LiMO<sub>2</sub>) of Li<sub>1.6</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> shows additional plateau below 2.8 V ( $Mn^{4+} \rightarrow Mn^{3+}$ ). The observed discharge capacity for the first cycle is as follows: 219 mAhg<sup>-1</sup> and 92.7 mAhg<sup>-1</sup> for Li<sub>1.44</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> and Li1.6Ni0.22 Co0.13Mn0.65O2 respectively. The cycling performance of the  $Li_x N_{i0.22} Co_{0.13} Mn_{0.65} O_2$  (x = 1.44, 1.6) electrode was compared as shown in Fig. 5. All the tested samples showed a gradual increase of discharge capacity during initial 5~8 cycles. J.H. Lim et al [17] firstly reported about this phenomenon of increasing capacity of Li2MnO3-LiMO<sub>2</sub> composite. All the prepared samples have good capacity retention during 11th cycle.

Both  $Li_xNi_{0.22}Co_{0.13}Mn_{0.65}O_2$  (x = 1.44, 1.6) materials prepared by Li content C-rat in Fig. 6. These discharge properties showed capacity retentions of 79% and 68% at 1C-rate compared with their capacities at 0.1 C-rate.  $Li_xNi_{0.22}Co_{0.13}Mn_{0.65}O_2$  (x = 1.44, 1.6) capacities were observed at x = 1.44 high c-rate value.

## Conclusion

Layered-layered composite electrode system of Lix

Table 2. Compositions of x in the Li<sub>x</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> cathode materials

Free Press	X 0.22 - 0.15 0.05 - 2.		
designed Li/M (M=Ni+Co+Mn)	Li/Ni/Co/Mn ratio experimental (AES-ICP)	alternative Li[M]O <sub>2</sub> notation	alternative $Li[M]O_2$ notation 2 (assumption : $Ni^{2+}$ , $Co^{3+}$ , $Mn^{4+}$ )
1.44	$Li_{1.44}Ni_{0.22}Co_{0.13}Mn_{0\cdot65}O_2$	$Li[Li_{0.3}Ni_{0.15}Co_{0.09}Mn_{0.45}]O_2$	$\begin{array}{c} 0.44 Li_2 MnO_3 \text{-} 0.56 Li \\ Ni_{0.46} Co_{0.28} Mn_{0.26} O_2 \end{array}$
1.6	$Li_{1.6}Ni_{0.22}Co_{0.13}Mn_{0\cdot65}O_2$	$Li[Li_{0.37}Ni_{0.14}Co_{0.8}Mn_{0.41}]O_2$	$\begin{array}{c} 0.6Li_2MnO_30.4Li\\ Ni_{0.55}Co_{0.32}Mn_{0.13}O_2 \end{array}$



**Fig. 5.** Cycling performances of (a) x = 1.44 and (b) x = 1.6 on x in the Li<sub>x</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> Li cell at a constant current density of 170 mA/g.



Fig. 6. Comparison of rate capabilities of (a) x = 1.44 and (b) x = 1.6 on x in the  $Li_xNi_{0.22}Co_{0.13}Mn_{0.65}O_2$  at different rates between 2.0 and 4.6 V.

Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> (x = 1.44, 1.6) positive-electrode material synthesis for lithium-ion batteries was synthesized via carbonate co-precipitation method. The XRD patterns of all the prepared powders show hexagonal  $\alpha$ -NaFeO<sub>2</sub> structure (space group: R-3m, 166) and existence of Li<sub>2</sub>MnO<sub>3</sub> phase in the composite structure. The morphology of the prepared powders has spherical agglomerates with the particle size varying from 5~8 µm. The initial

charge capacity in particular at 4.45 V increases with an increase of the amount of Li (Li<sub>2</sub>MnO<sub>3</sub>) except for Li<sub>1.44</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub>. The observed charge and discharge capacity for the first cycle is 298.5, 219 mAhg<sup>-1</sup> for Li<sub>1.44</sub>Ni<sub>0.23</sub>Co<sub>0.12</sub>Mn<sub>0.65</sub>O<sub>2</sub>, respectively. The poor charge-discharge capacity of Li<sub>1.6</sub>Ni<sub>0.22</sub>Co<sub>0.13</sub>Mn<sub>0.65</sub>O<sub>2</sub> may result from relatively small amount and high oxidation state of M (LiMO<sub>2</sub>) because it is not sufficient to a Li<sub>2</sub>MnO<sub>3</sub> electrode to electrochemical cycling when charged to high potential.

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