



Co-precipitation synthesis of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor and characterization of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material for secondary lithium batteries



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ABSTRACT

$\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials were synthesized from spherical and homogeneous mixed metal hydroxide $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ which was prepared by co-precipitation method. The synthetic conditions of the metal hydroxide, such as pH, amount of chelating, stirring speed, temperature, etc. were studied in detail. The homogeneous and spherical $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor obtained in the optimized synthetic conditions had a high tap-density of 1.94 g cm^{-3} . A well-ordered layer-structured and spherical $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material, with the tap-density of 2.59 g cm^{-3} , was fabricated by calcinating the as-prepared $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor and 5% excess $\text{LiOH}\cdot\text{H}_2\text{O}$ at 820°C in the flowing oxygen. The crystal structure, morphology and electrochemical properties of the precursors and final products were investigated by using X-ray diffractometry, scanning electron microscopy, charge-discharge test and C-V method. In the voltage ranges of 2.8–4.3, 4.4 and 4.5 V, the initial discharge capacities of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ at 1 C rate were 172.1, 177.9 and 182.5 mAh g^{-1} , respectively, while the corresponding discharge capacity retention ratios after 100 cycles were 94.3%, 90.7% and 85.4%. For elevated temperature operation (60°C), the resulted capacity was as high as 196.9 mAh g^{-1} in the voltage range of 2.8–4.3 V and retained 89.7% after 100 cycles.

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1. Introduction

Because of the drawbacks of LiCoO_2 , such as high cost, toxicity of cobalt and so on, research and development of new cathode materials for lithium ion batteries are ongoing to replace it, for example, layered LiNiO_2 [1,2], LiMnO_2 [3,4] and spinel LiMn_2O_4 [5,6]. However, stoichiometric LiNiO_2 is difficult to synthesize and also known for its poor cycling characteristic resulted from its two major material defects: its tendency to non-stoichiometry caused by Li/Ni cations displacement during the synthesis process and its structural instability during lithium intercalation/de-intercalation process [7–9]. LiMnO_2 with layered structure has a high theoretical specific capacity. However, during the process of charging and discharging, the layered structure of LiMnO_2 easily changes to the spinel structure, resulting in fast attenuation of capacity [10]. LiMn_2O_4 presents smaller capacity, and significant capacity fading during cycling at elevated temperature due to manganese dissolution, electrolyte decomposition and Jahn–Teller distortion [11,12].

Therefore, various approaches such as partial replacement of nickel and manganese by transition metals, surface coated, optimizing preparation methods and conditions are adopted to improve their performance [4,13–16].

$\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ series, which integrate features of LiCoO_2 , LiNiO_2 and LiMnO_2 , have attracted more attentions for their high capacity, low cost, good cycling stability and safety [17–22]. In the series, Ni provides a high capacity but poor thermal stability, while Mn maintains an excellent cycling performance and safety. And Co offers increased electronic conductivity resulting in an excellent rate capability. Now $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ have been commercialized and used widely in commercial lithium-ion batteries. However, the capacity of these materials are not high enough ($150\text{--}160 \text{ mAh g}^{-1}$) [23,24]. Various methods have been applied to synthesize $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode materials, such as hydroxide co-precipitation method [25–30], carbonate co-precipitation method [31,32], combustion method [33], solid-state method [34–36] and spray-drying method [34,37,38]. Cao et al. [25] prepared $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ by co-precipitation method that delivers an initial discharge capacity of 175.3 mAh g^{-1} in the voltage of 2.75–4.3 V at 1 C rate, and over 151.2 mAh g^{-1} after 70 cycles. However, it dropped dramatically in the following cycles.

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Li et al. [26] prepared $\text{LiNi}_{0.6}\text{Mn}_{0.4-x}\text{Co}_x\text{O}_2$ ($x = 0.05, 0.1, 0.15, 0.2$) and found the sample with $x = 0.2$ delivered an initial discharge capacities of $170\text{--}175\text{ mAh g}^{-1}$ and only 71.5% was remained after 50 cycles at 30 mA g^{-1} in the voltage of $2.5\text{--}4.3\text{ V}$. Liao et al. [27] synthesized $\text{LiNi}_{0.6}\text{Co}_{0.4-x}\text{Mn}_x\text{O}_2$ ($x = 0.15, 0.2, 0.25$) materials by calcining a mixture of $\text{Ni}_{0.6}\text{Co}_{0.4-x}\text{Mn}_x(\text{OH})_2$ and Li_2CO_3 in flowing oxygen atmosphere. The samples for $x = 0.2$ calcined at 940°C delivered an initial discharge capacity of 175.6 mAh g^{-1} and a capacity retention of 96.6% after 20 cycles at 30 mA g^{-1} in the voltage of $3.0\text{--}4.3\text{ V}$. Chen et al. [28] prepared $\text{LiCo}_x\text{Mn}_y\text{Ni}_{1-x-y}\text{O}_2$ ($0 \leq x \leq 0.3$, and $y = 2$) by heating a mixture of $\text{Co}_x\text{Mn}_y\text{Ni}_{1-x-y}(\text{OH})_2$ and Li_2CO_3 at $850\text{--}900^\circ\text{C}$ for 24 h in air. They reported that $\text{LiCo}_{0.1}\text{Mn}_{0.2}\text{Ni}_{0.7}\text{O}_2$ and $\text{LiCo}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.6}\text{O}_2$ had the best electrochemical characteristics and their initial discharge capacities attained 150 mAh g^{-1} at the current of 0.4 mA cm^{-2} between 3.0 and 4.3 V and no cycle performance was mentioned in this paper. Yue et al. [30] have reported that $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ prepared by mixture of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ and $\text{LiOH}\cdot\text{H}_2\text{O}$, preheated at 500°C for 5 h and then heated at 800°C for 15 h in air, could deliver an initial discharge capacity of 169.8 mAh g^{-1} and 148.9 mAh g^{-1} at $0.1, 1\text{ C}$ rate, respectively, in the voltage of $2.8\text{--}4.3\text{ V}$, with only 89.2% of the initial discharge capacity was remained after 50 cycles at 1 C rate.

So it can be found that the main problems of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ cathode material are low capacity at high rate and poor cycle performance. And few group studied the preparation conditions systematically and paid attention to the tap-density and particle morphology of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor. In addition, less attention has been paid to the long life cyclicity at high current rates and performance at high temperature. In this research, the optimum conditions for preparation of spherical $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ were studied in detail, such as pH, the amount of chelating agent, stirring speed and temperature, etc. The structural properties, morphology, electrochemical properties of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ powders were also investigated thoroughly.

2. Experimental

$\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor was synthesized by the co-precipitation method. $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4\cdot \text{H}_2\text{O}$ were used as starting materials and were dissolved in distilled water in a molar ratio of $\text{Ni}^{2+} : \text{Co}^{2+} : \text{Mn}^{2+} = 6 : 2 : 2$. A 1.5 M aqueous solution of transition metal sulfates was slowly pumped into a continuous stirred tank reactor (capacity 10 L) under nitrogen atmosphere. At the same time, a 4 M NaOH solution(aq) and appropriate amount of NH_4OH solution(aq) as chelating agent were also separately pumped into the reactor. After reaction, the precipitate was filtered and washed several times to remove the residual ions (Na^+ , SO_4^{2-} or other ions). The precipitate was then dried at 80°C overnight. The concentration of the solution, pH,

amount of NH_4OH , stirring speed and temperature in the reactor were carefully controlled.

The obtained precursor of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ and 5% excess $\text{LiOH}\cdot\text{H}_2\text{O}$ were mixed thoroughly in an agate mortar. The mixture was first calcined at 550°C for 4 h in air, and then heated at $780, 820$ and 860°C for 12 h in flowing oxygen atmosphere to obtain $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ powders.

The synthesized compounds were characterized by using X-Ray diffraction (XRD)(Rigaku θ/θ diffractometer with $\text{Cu K}\alpha$ radiation($r = 1.54056\text{ \AA}$)). XRD datas were obtained at $2\theta = 10\text{--}80^\circ$, with a scan speed of 2° min^{-1} . The morphological features and particle sizes were observed by scanning electron microscope equipped with EDXS energy disperse X-ray spectrometer(SEM, Hitachi X-650). The chemical compositions of the resulting compounds were analyzed by atomic absorption spectroscopy (AA spectrophotometer, Zhimadu 6650).

The charge/discharge tests were carried out by assembling 2025-type coin cells with a lithium metal anode, working cathode and Celgard 2400 microporous membrane. The working cathode was fabricated by 80 wt% $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$, 10 wt% acetylene black and 10 wt% PVDF binder. A 1 mol L^{-1} solution of LiPF_6 dissolved in ethylene carbonate (EC)/dimethyl carbonate(DMC)(1:1,v/v) was employed as the electrolyte. The charge-discharge tests were set to be charged and discharged between 2.8 and 4.3 V at 0.1 C rate in the first 2 cycles and then at 1 C rate in the following 100 cycles at 25°C or 60°C . Cyclic voltammograms measurements were done by a Solartron 1287 electrochemical interface between 2.8 and 4.5 V at a scan rate of 0.1 mV s^{-1} .

3. Results and discussion

3.1. Optimization of synthetic conditions of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$

The tap-density of the powders is closely related to the powders' particle morphology, particle size and particle size distribution, etc. The powders composed of spherical particles have higher tap-density than the powders composed of irregular particles. The spherical $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor with a very homogeneous distribution of Ni^{2+} , Co^{2+} and Mn^{2+} on the atomic scale can also be synthesized via the co-precipitation method[23,39]. Additional, it is easier to synthesize $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ from $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ precursor because the layered structure of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ and $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ are very similar, as has been indicated by the X-ray diffraction patterns. In this research, four critical factors for synthesizing uniform and spherical $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ particles were studied ordinally. Eleven samples were prepared at different pH, concentration of NH_4OH , stirring speed and temperature. P_i ($i = 1, 2, 3, \dots, 11$) was used to

Table 1
Preparation conditions of $\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$ powders.

Sample	pH	Concentration of NH_4OH (mol L^{-1})	Stirring speed(rpm)	Temperature($^\circ\text{C}$)	Tap-density (g cm^{-3})	
					$\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$	$\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$
P1	11.2	1.0	600	50	1.65	2.29
P2	11.5	1.0	600	50	1.47	2.08
P3	11.8	1.0	600	50	1.08	1.62
P4	11.2	0.3	600	50	1.29	1.78
P5	11.2	0.6	600	50	1.76	2.37
P6	11.2	1.0	600	50	1.66	2.27
P7	11.2	0.6	400	50	1.48	2.05
P8	11.2	0.6	600	50	1.78	2.39
P9	11.2	0.6	800	50	1.91	2.55
P10	11.2	0.6	800	55	1.94	2.59
P11	11.2	0.6	800	60	1.89	2.52

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