

Controllable Synthesis of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ By a Co-precipitation Method

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Abstract. Composite metal hydroxide $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ has been prepared via a co-precipitation reaction method. The obtained powders show a single phase with a typical hexagonal phase of $\beta\text{-Ni}(\text{OH})_2$. SEM reveals that the irregular secondary $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ particles were formed at the initial stage and the irregular particles changed gradually into spherical particles with the increase in the reaction time. The $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode, synthesized using as-prepared $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ as the precursor, has an initial discharge capacity of 162.4 mAh g^{-1} and the discharge capacity still keeps 156.3 mAh g^{-1} at 50th cycle.

Introduction

LiCoO_2 is widely used as a positive electrode material for lithium secondary batteries because of its simple synthesis and excellent cycle performance [1]. However, the toxicity and high cost of cobalt has made researchers exploit alternative cathode active materials for Li ion batteries. Mixed metal oxide $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ used as the cathode material in lithium ion batteries has been extensively investigated due to its high capacity, good thermal stability and relatively low cost compared with LiCoO_2 [2]. The theoretical capacity of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ was determined to be 278 mAh g^{-1} and the practically attainable capacity was found to be over 160 mAh g^{-1} in the voltage range 2.5-4.3 V [3].

$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ is a layer-structured oxide that is isostructural with LiCoO_2 and LiNiO_2 ($\alpha\text{-NaFeO}_2$ structure, R-3m space group), which has a close-packed network of oxygen atoms with Li^+ ions and transition metal ions (Ni^{2+} , Ni^{3+} , Co^{3+} and Mn^{4+}) ordering of alternating planes of cubic structure [4]. In $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$, it is assumed that the predominant valence states for the metal ions are Ni^{2+} , Ni^{3+} , Co^{3+} , Mn^{4+} with small content of Mn^{3+} ions. It was shown that the electrochemical process in the range 2.5-4.4 V versus Li involves the two-electron transfer reaction as $\text{Ni}^{2+} \leftrightarrow \text{Ni}^{4+}$ and one-electron transfer reaction as $\text{Ni}^{3+} \leftrightarrow \text{Ni}^{4+}$ in addition to $\text{Co}^{3+/4+}$ for small values.

The synthesis method has a strong effect on the physical properties (morphology, particle size distribution, tap density and specific surface area) and electrochemical performance of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode material [5]. $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ was prepared by a carbonate co-precipitation method [6], sol-gel method and solid state reaction [7, 8]. Some of earlier research groups have reported that employing co-precipitation to prepare metal hydroxide would be the best choice, because the method essentially gives phase-pure oxide products. The structural and electrochemical properties of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ synthesized by the hydroxide co-precipitation method are greatly related to its precursor $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$.

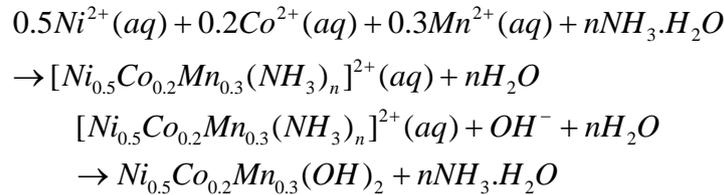
In the present study, spherical $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ powders was prepared via a co-precipitation reaction method, which is powerful technique to prepare a cathode material precursor by which we can not only easily get the homogeneous mixing of transition metal ion at an atomic level, but also

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freely control the composition of compound. The structural and physiochemical behaviors of this compound were investigated.

Experimental

The formation of composite metal hydroxide is according to the following reaction:



All the reagents were purchased from commercial sources and used without further purification. For the co-precipitation reaction, stoichiometric amounts of $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot 4H_2O$ were weighed and dissolved together in deionized water (transition metal ratio of Ni:Co:Mn=5:2:3), and the concentration of the total metal sulfate was controlled at 2 mol L^{-1} . A proper amount of deionized water was added to a specially designed reaction tank, heated to $60 \text{ }^\circ\text{C}$, and strongly stirred until the end of the reaction. The mixed metal solution was added to the reaction tank under nitrogen atmosphere. At the same time, 2.0 mol L^{-1} NaOH solution and desired amount of $NH_3 \cdot H_2O$ solution as chelating agents were separately fed into the reaction tank. The concentration of the solution, pH (10.5), temperature ($60 \text{ }^\circ\text{C}$), and stirring speed (1000 rpm) in the reaction tank were all carefully controlled. Then, the precipitates were filtered and washed with deionized water. The obtained powers were dried in air at $100 \text{ }^\circ\text{C}$ to remove adsorbed water.

The X-ray diffraction (XRD) measurement was carried out with a Bruker D8 Advance X-ray diffractometer (Germany) with $Cu-K\alpha_1$ radiation ($\lambda=1.54056\text{\AA}$). Data was collected between 10° and 80° with a scan speed of $4^\circ/\text{min}$. The particle size and morphological features were revealed by scanning electron microscope (SEM, JEOL JSM-6700F, Japan). The particle size distribution was obtained using a laser granulometer (Malvern, model Mastersizer 2000), and water was used as the dispersing agent.

The charge/discharge tests were carried out using the coin-type cell (size: 2016), which used $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ sample, synthesized using as-prepared $Ni_{0.5}Co_{0.2}Mn_{0.3}(OH)_2$ as the precursor, as the working electrode and a lithium foil as the counter electrode. Working electrode was fabricated by mixing 85wt% $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ powders with 8wt% acetylene black and 7wt% PVDF binder, coating the mixture onto an aluminum foil current collector. The electrolyte was the solution of 1 mol L^{-1} $LiPF_6$ dissolved in EC/DMC (1:1 volume ratio). A porous polypropylene film (Celgard 2300) was used to separate two electrodes. The cells were assembled in an argon-filled Unilab-2000 glove box (Mbraun, Germany). The cells were charged and discharged between 2.5~4.3V versus Li/Li^+ at a constant current density of 30 mA g^{-1} then at a constant voltage of 4.3V. All the electrochemical measurements of the cells were performed at room temperature on a Neware battery test system (Newell, China).

Results and discussion

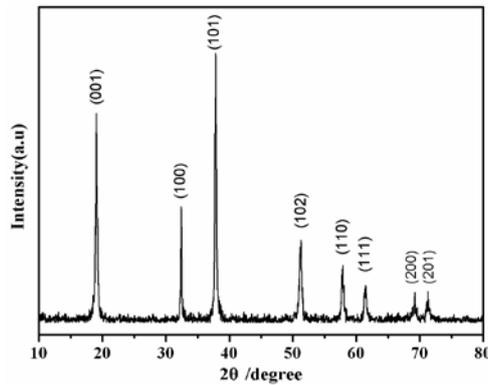


Fig. 1. XRD patterns of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ powders

XRD pattern of as-synthesized $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ is presented in Fig. 1. The sharp and strong diffraction peaks indicate that the sample is well crystallized. No impurity phases are detected in this sample. All diffraction peaks of this sample can be perfectly indexed as the typical hexagonal phase of $\beta\text{-Ni}(\text{OH})_2$ (JCPDS, file No. 14-0117). No peaks from impurities are observed, indicating that the product is pure phase and that Ni, Co, and Mn are homogeneously distributed within $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ particle. The crystal lattice parameter of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$, calculated by means of least-square method in terms of hexagonal space group, is $a=b=3.1898$, $c=4.6431$.

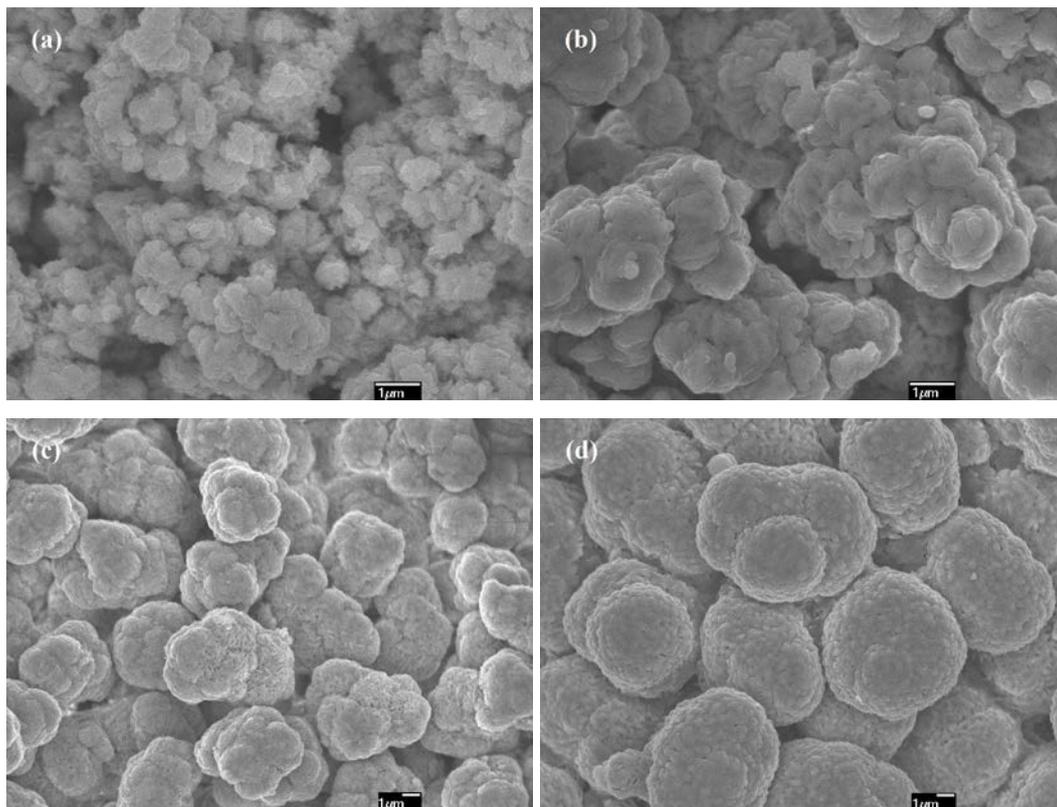


Fig. 2. SEM images of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ powders prepared for: (a) 1 h; (b) 5 h; (c) 10 h and (d) 24 h.

Morphology control is essential to electrochemical property of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ positive material, and morphology of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ is greatly related to the morphology of its precursor. Fig. 2 presents the SEM images of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ prepared at different reaction time. The particle size is relatively uniform and increases with increasing the reaction time. The $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ sample prepared in 1 h is composed of irregular secondary particles formed by aggregated primary crystallites (rod shaped grains). When the reaction time increases to 5 h, relatively rounded contour particles are formed as a result of closely piled primary grains. Apparently,

the sample prepared for 10 h comprises of semi-spherical secondary particles. Each of semi-spherical particles is composed of closely piled primary rod-like grains with an average diameter of about 0.2 μm and an average length of about 0.5 μm . As the reaction time is prolonged to 24 h, spherical $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ is formed. As seen from Fig.2 (d), the spherical $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ particles have a larger particle size (average size about 7.61 μm) and narrower particle size distribution, which is quite useful for further processing.

Apparently, at the initial stage of the co-precipitation reaction, the irregular secondary particles formed by the agglomeration of the primary rod-like grain were formed and the irregular particles grew progressively and changed gradually into spherical particles with the increase in the reaction time.

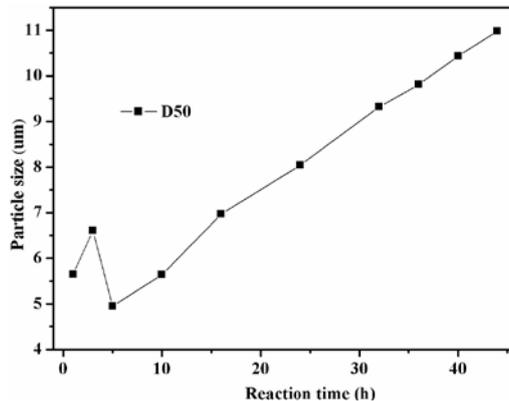


Fig. 3. Particle size distribution of the $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ powders.

Fig. 3 shows the particle size distribution of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ prepared at different reaction time. The D50 of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ sample prepared in 1 h is about 5.65 μm , which is obviously larger than particle size of SEM shown in Fig. 4(a). The reason is that those irregular secondary particles were softly agglomerated into larger ones and such agglomerates could not be separated during particle size measurement process. The D50 of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ sample prepared in 5 h is about 4.95 μm , smaller than that of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ samples prepared in 1 h and 3 h, due mainly to the alleviation of undesired agglomeration of secondary particles for $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ sample prepared in 5 h. The particle size of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ sample increases monotonously after 5 h, as seen from Fig.4 and Fig.5. The D50 of $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ sample prepared in 24 h was 8.04 μm , which is almost identical to that of SEM shown in Fig. 4(d), indicating that this sample have good dispersivity and fluidity.

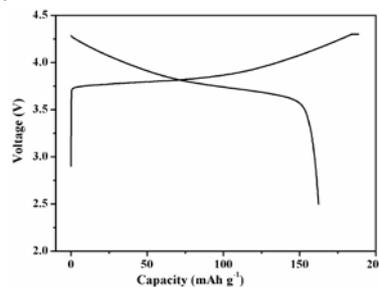


Fig. 4. The first discharge-charge curve of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ between 2.5 and 4.3 V.

$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ sample was prepared by solid-state reaction using as-prepared $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ as the precursor. Fig. 4 shows the initial charge-discharge curves of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode at a moderate current density of 30 mA g^{-1} between 2.5 and 4.3 V then at a constant voltage of 4.3V. The initial charge capacity is 188.5 mAh g^{-1} . The initial discharge capacity is 162.4 mAh g^{-1} , and the initial coulombic efficiency is 86.2%. The initial irreversible capacity for this $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ is 26.1 mAh g^{-1} , which mainly results from oxidation decomposition of electrolyte occurring mainly on the surface of the cathode material at high potentials in the charge process.

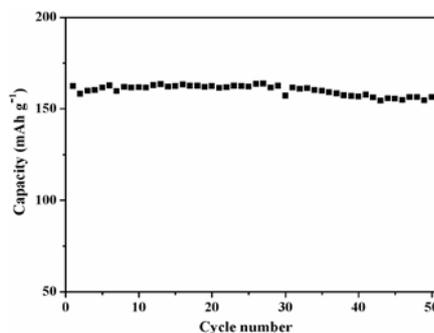


Fig. 5. Cycling performance of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ between 2.5 and 4.3V

The cycling performance of this $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ sample at a current density of 30 mA g^{-1} between 2.5 and 4.3 V then at a constant voltage of 4.3V is shown in Fig.5. As seen from Fig. 5, as-obtained $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ electrode displays good cycling performance. The discharge capacity of this $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ still keeps 156.3 mAh g^{-1} at 50th cycle. The discharge capacity retention from the first to the 50th is around 88.9% with an average capacity fade rate around 0.07% per cycle. The efficiency of the Li insertion/deinsertion processes gradually increases and reaches 99% from 3 cycles.

Conclusions

Co-precipitation reaction was used for synthesizing $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ precursor. XRD studies showed that as-prepared $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ had well-ordered $\beta\text{-Ni}(\text{OH})_2$ structure. SEM studies showed that the irregular secondary particles were formed at the initial stage and the irregular particles changed gradually into spherical particles with the increase in the reaction time. The particle size of as-obtained $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ increased progressively and the secondary particles became dispersive with increasing the reaction time. Electrochemical tests indicated that the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode, which was prepared by solid-state reaction using as-prepared $\text{Ni}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{OH})_2$ as the precursor, could deliver high special capacity and good cycling stability.

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