

Preparation of layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ as positive material for lithium-ion secondary battery

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Abstract: The uniform layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cathode material for lithium-ion secondary batteries were synthesized by using $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$ synthesized by a liquid phase co-precipitated method as precursors and with NiSO_4 , CoSO_4 , MnSO_4 and $\text{NH}_3\cdot\text{H}_2\text{O}$ as raw materials. The influence of the preparation conditions such as precursors preparation, calcinations temperature and calcinations time on the structural and electrochemical properties of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ were systematically studied. The result of XRD shows the I_{003}/I_{104} value of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder synthesized at 950 °C for 10 h is 1.26, which illustrates the well-ordered layer-structure. The average particle size of uniform $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder is about 400 nm in diameter as observed by scanning electron microscopy. The first discharge capacity of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ electrode is 174.6 mA·h/g at 16 mA/g between 2.8 V and 4.5 V versus Li at room temperature, and the capacity retention is 95.2% of the initial discharge capacity after 50 cycles at 32 mA/g.

Key words: Co-precipitation method; $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$; positive materials; lithium ion batteries

1 Introduction

LiCoO_2 is the mostly wide used positive material in commercial secondary batteries, as it is easy to prepare and has good recharge ability even at high rate performances. However, the toxicity and high cost of cobalt represent some of the problems of this material. Therefore, extensive research has been carried out to find alternative positive electrode materials such as LiFePO_4 [1–2] and LiMn_2O_4 [3–4].

Recently, the layer-structural $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ compound has been considered as a promising candidate of next-generation cathode materials to replace LiCoO_2 for rechargeable lithium ion batteries due to its large capacity and stable structure[5–10]. The layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ material could be synthesized with various methods such as hydroxide co-precipitation route[5, 7, 11], carbonate co-precipitation route [12–13], oxalate co-precipitation route[14–15] and all solid state method[16]. The structure stability and the cycling performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ could be improved by doping or substituting various ions such as Cr[17],

Al[18–19], and F[15–18]. However, the preparation of the homogeneous $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ is not easy. Selecting a suitable preparation route is important for obtaining phase-pure final products. In the present work, $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ is synthesized by mixing the co-precipitation metal hydroxide $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$ with 8% excess $\text{LiOH}\cdot\text{H}_2\text{O}$ followed by heat-treatment; the influence of the preparation conditions of $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$, the calcinations temperature and time on the structure and electrochemical properties of the $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$ are studied in detail.

2 Experimental

In order to prepare a homogeneous precursor $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$, we applied the hydroxide co-precipitation method as LEE et al reported[6]. An aqueous solution consisting of the $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4\cdot \text{H}_2\text{O}$ (cationic ratio of $\text{Ni:Co:Mn}=1:1:1$) with a concentration of 2 mol/L was precipitated by adding NaOH solution (aq.) of 2 mol/L and a desired amount of $\text{NH}_3\cdot\text{H}_2\text{O}$ solution (aq.) separately under argon atmosphere along with continued

stirring. The solution was maintained at 60 °C for 12 h and the pH was controlled to 11–12. Then, the spherical precursor was filtered, washed and dried in a vacuum at 100 °C for 12 h. The obtained precursor powder was mixed with 8% excess LiOH·H₂O (excess amount of Li salts was used to compensate for possible Li loss during the calcinations) thoroughly using a ball mill. The mixture was initially heated to 480 °C for 5 h and then calcined at 850–950 °C for 8–20 h in air to obtain Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂.

Powder X-ray diffraction was carried out using a Cu K_α radiation of Rigaku D/max 2550 diffractometer. Scanning electron micrographs(SEM) was used to characterize the images of the prepared powder.

The cathode was prepared by mixing the active material with carbon black and PVDF in a mass ratio of 90.5:3.5:6.0. The R2025 cells consisting of the cathode, the lithium foil using as the anode and the electrolyte of 1 mol/L LiPF₆ ethylene carbonate(EC)-dimethylene carbonate(DMC)-ethylmethyl carbonate(EMC) (1:1:1 in mass) were assembled in an argon-filled glove box. Cycle tests were performed on the cells between 2.8 V and 4.5 V at 16 mA/g and 25 °C with a BK6061 Testing System (160 mA/g was assumed to be 1 C rate).

3 Results and discussion

3.1 Phase structure of precursors

The obtained brown colored powder from the hydroxide co-precipitation process was used as precursors. Three precursors of (Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)₂ were prepared with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{transition metal cation}, \text{TM}=\text{Ni, Co, Mn})=1.0:1, 1.5:1$ and $2.0:1$ (molar fraction), and were referred as S10, S15 and S20. Fig.1 shows the XRD patterns of the precursor (Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)₂. As being seen in Fig.1, the X-ray diffraction pattern of the precursor prepared with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{TM cation})=1.5:1$ shows broad integrated lines and a high peaks at around $2\theta=19^\circ$, which can be attributed to TM hydroxides. Fig.2 shows the scanning electron micrographs(SEM) images for the precursor S15. The results show an uniform hydroxide co-precipitation, (Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)₂, was successfully prepared.

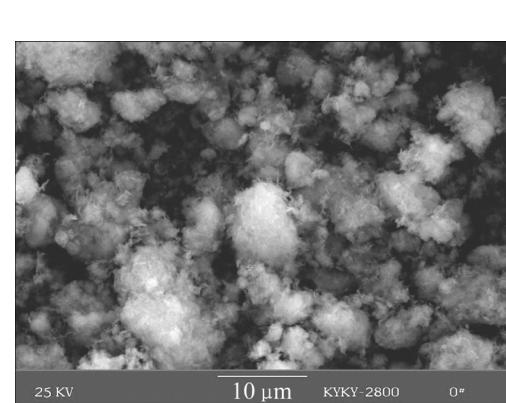


Fig.2 SEM image of precursor (Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)₂ synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.5:1$

3.2 Phase structure and electrochemical properties of Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂

Fig.3 illustrates the powder's X-ray diffraction patterns of the Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ samples prepared with different precursors at 900 °C for 10 h. All the samples can be indexed to the hexagonal α -NaFeO₂ structure (space group: $R\bar{3}m$). As seen in Fig.3, the splits in the (006)/(012) and (018)/(110) doublets can be observed in all the XRD patterns, respectively in the X-ray curve of Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ synthesized with precursor S15. The results show that the layered Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ cathode materials have been successfully synthesized with all the precursors though the samples synthesized with precursors S14 and S20 show the bad (006)/(012) doublets. Some researchers[20]

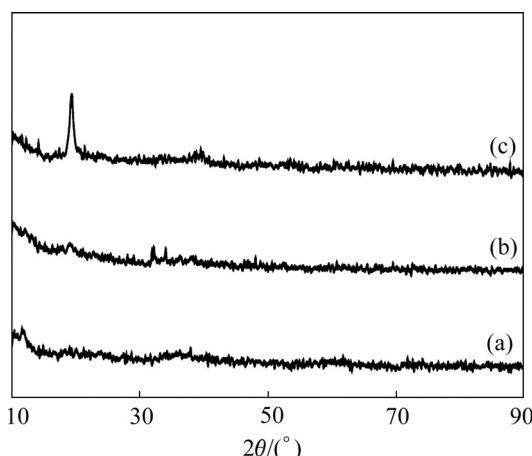


Fig.1 X-ray diffraction patterns of (Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)₂ prepared with different ratios of $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})$: (a) 1.0:1; (b) 2.0; (c) 1.5

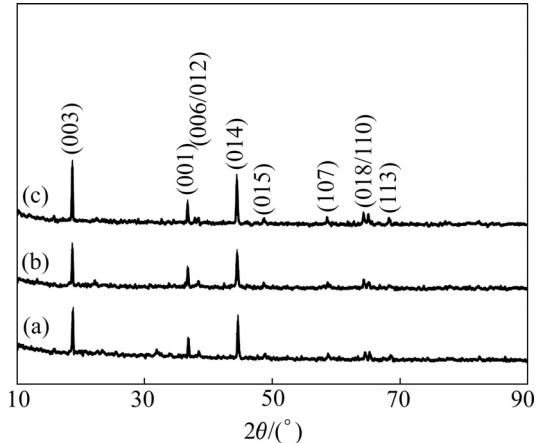


Fig.3 X-ray diffraction patterns of Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ powder synthesized with different precursors at 900 °C for 10 h (Precursors (Ni_{1/3}Co_{1/3}Mn_{1/3})(OH)₂ prepared with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.0:1$ (a), 2.0:1 (b) and 1.5:1 (c))

used the high integrated intensity ratio of the I_{003}/I_{104} to indicate the cation mixing of the layered structure. Generally, when $I_{003}/I_{104} > 1.2$, the cathode materials has a good layered structure due to the small cation mixing. The I_{003}/I_{104} values of the three samples synthesized with precursor S10, S20 and S15 are 1.17, 1.09 and 1.2 in this work, which shows only the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with precursors S15 at 900 °C for 10 h formed good layer structure.

In order to further study the influence of the preparation conditions of the precursors on the electrochemical performance of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, the tests cells were operated at a constant current density of 16 mA/g between 2.8 V and 4.5 V versus Li at room temperature. Fig.4 shows the initial charge/discharge curves of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders synthesized with the three precursors at 900 °C for 10 h. As seen from Fig.4, the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ prepared with precursor S15 shows quite smooth and monotonous charge/discharge curves. On charging at 16 mA/g, voltage suddenly increases to about 3.75 V and then hold on 3.75–3.9 V until the charge capacity reaches about 115 mA·h/g, which can be attributed to the $\text{Ni}^{2+}/\text{Ni}^{4+}$ redox reaction occurred in this region[17]. On the further charging, the voltage curves monotonously increases to 4.5 V. Charge-discharge capacities and capacity retention ratios of all the samples are listed in Table 1. The $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ prepared with precursor S15 shows the highest charge capacity of 190 mA·h/g and discharge capacity of 160.9 mA·h/g in the first cycle, for which the efficiency corresponds to 84.75%. The discharge capacities of 71.7 mA·h/g and 107.4 mA·h/g are obtained at the first cycle for $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ prepared with the precursor S10 and precursor S20.

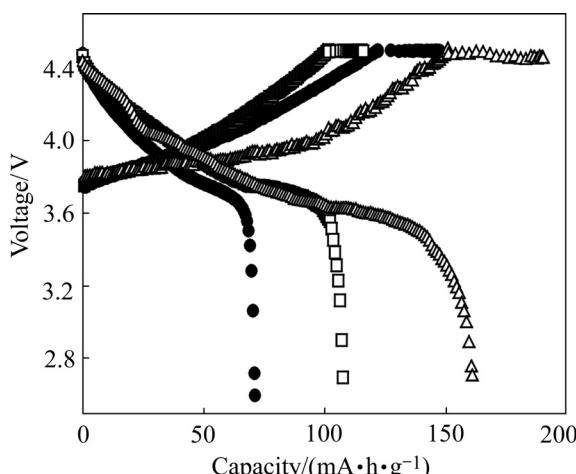


Fig.4 Initial charge-discharge profiles of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with different precursors at 900 °C for 10 h and 16 mA/g at 30 °C (Precursors prepared with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.0:1$ (a), 2.0:1 (b) and 1.5:1 (c))

Table 1 Charge-discharge capacity of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with various precursors at 900 °C for 10 h

$n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})$	First charge capacity/ (mA·h·g⁻¹)	First discharge capacity/ (mA·h·g⁻¹)	First discharge efficiency/%
1.0:1	148.8	71.7	48.2
2.0:1	115.9	107.4	92.7
1.5:1	190.0	160.9	84.7

Fig.5 demonstrates the X-ray diffraction pattern of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder synthesized with precursors S15 at various temperatures for 10 h. As seen in Fig.5, the splits in the (006)/(102) and (018)/(110) doublets are observed in all the XRD patterns. The I_{003}/I_{104} values of the samples calcined at 850, 900 and 950 °C are calculated as 1.59, 1.2 and 1.26. The I_{003}/I_{104} values of all samples synthesized with precursors S15 are larger than 1.2. The results show that the desirable good layer structure of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ prepared are obtained.

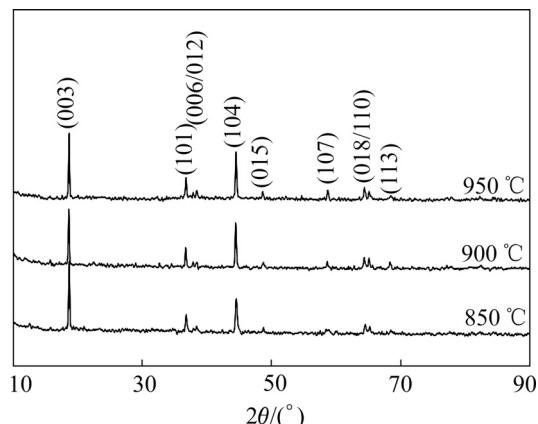


Fig.5 X-ray diffraction pattern of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.5:1$ at various temperatures for 10 h

Fig.6 shows the initial charge/discharge curves of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders synthesized with precursor S15 at various temperature for 10 h. The charge-discharge capacities of all the samples are listed in Table 2. The results show that the sample synthesized at 950 °C for 10 h delivers the highest discharge capacity of 174.6 mA·h/g and the largest discharge efficiency of 90.3% in the first charge- discharge cycle.

Fig.7 illustrates the X-ray diffraction pattern of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder synthesized with the precursors S15 at 950 °C for various calcinations time. The I_{003}/I_{104} values of the samples synthesized at 950 °C for 8, 10, 15 and 20 h are 1.23, 1.26, 1.16 and 1.24, which reveal that the powder of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized at 950 °C for 10 h has the better layer

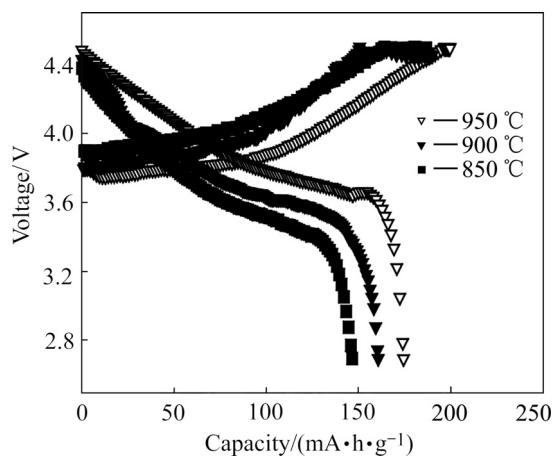


Fig.6 Initial charge-discharge profiles of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ ($2.8\text{--}4.5\text{ V}$) synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.5:1$ at various temperatures for 10 h and operated in 16 mA/g at 30 °C

Table 2 Charge-discharge capacity of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.5:1$ at various temperatures for 10 h

Temperature/ °C	First charge capacity/ (mA·h·g ⁻¹)	First discharge capacity/ (mA·h·g ⁻¹)	First discharge efficiency/ %
850	186.9	146.7	78.5
900	190.0	160.9	84.7
950	193.4	174.6	90.3

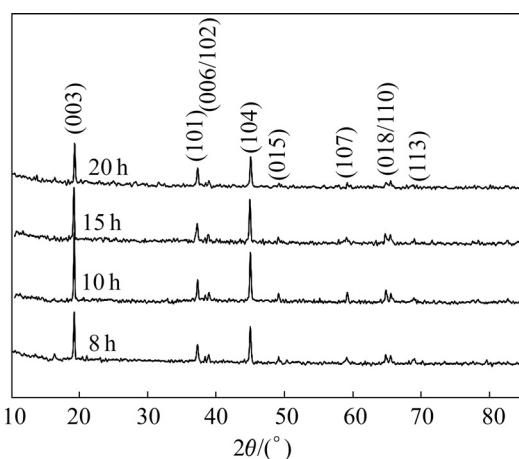


Fig.7 X-ray diffraction patterns of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.5:1$ at 950 °C for various time

structure.

The initial charge-discharge curves of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder prepared with precursor S15 at 950 °C for various calcination time are shown in Fig.8. The charge-discharge capacities and retention ratios of all of the samples are tabulated in Table 3. The

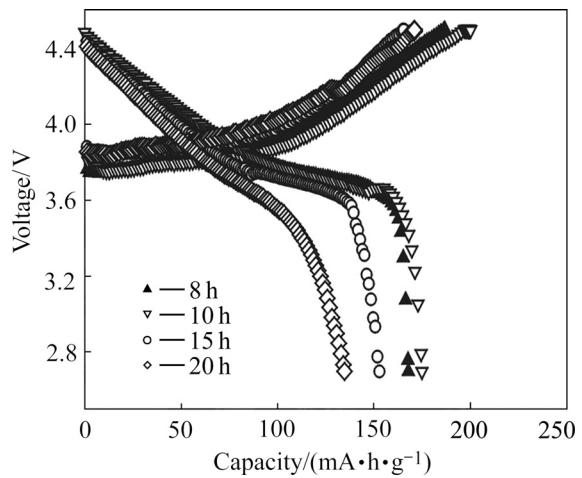


Fig.8 Initial charge-discharge profiles of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.5:1$ at 950 °C for various time at 16 mA/g and 30 °C

Table 3 First Charge-discharge capacity of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}\text{-Co}^{2+}\text{-Mn}^{2+})=1.5:1$ at 950 °C for different time

Time/ h	First charge capacity/ (mA·h·g ⁻¹)	First discharge capacity/ (mA·h·g ⁻¹)	First discharge efficiency/ %
8	186.4	167.6	89.9
10	193.4	174.6	90.3
15	185.2	152.6	82.4
20	170.9	134.5	78.7

results show the sample synthesized at 950 °C for 10 h delivers the higher discharge capacity in the first cycle at 16 mA/g at room temperature. The discharge capacity of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ in the first cycle decreases with the increase of calcination time at 950 °C.

Fig.9 shows the discharge capacities as a function of cycle number of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with precursors S15 at 950 °C for various time at 32 mA/g. The results show that the reversible capacities of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ material after 50 cycles at 32 mA/g are 149.8 mA·h/g (89.4% of the initial discharge capacity), 166.6 mA·h/g (95.4% of the initial discharge capacity), 116.7 mA·h/g (76.5% of the initial discharge capacity) and 103 mA·h/g (76.6% of the initial discharge capacity) when calcinations time at 950 °C are 8, 10, 15 and 20 h, respectively. The results show that the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder synthesized with precursors S15 at 950 °C for 10 h delivers the better layered structure and the better electrochemical properties, such as the higher discharge capacity of 174.6 mA·h/g at the first cycle, the larger capacity retention of

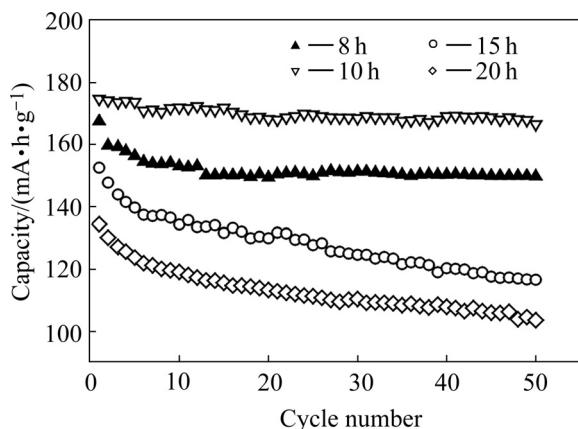


Fig.9 Discharge capacities as function of cycle number of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}-\text{Co}^{2+}-\text{Mn}^{2+})=1.5:1$ at $950\text{ }^\circ\text{C}$ for various time

95.4% after 50 cycles at 32 mA/g.

Fig.10 shows the scanning electron micrographs (SEM) images for the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with precursors S15 at $950\text{ }^\circ\text{C}$ for 10 h. It can be seen the average particle size of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ is nearly 400 nm and homogenous $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ are successfully synthesized.

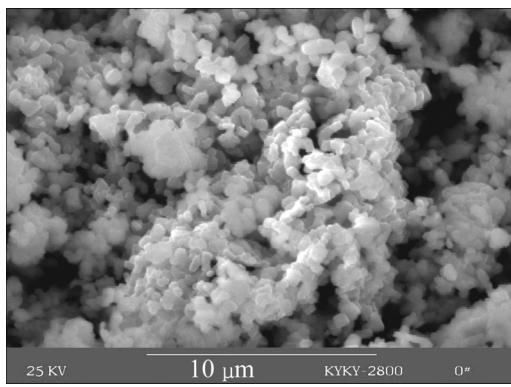


Fig.10 SEM image of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{Ni}^{2+}-\text{Co}^{2+}-\text{Mn}^{2+})=1.5:1$ at $950\text{ }^\circ\text{C}$ for 10 h

4 Conclusions

A uniform co-precipitation melted hydroxide $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$ is successfully prepared with $n(\text{NH}_3\cdot\text{H}_2\text{O}):n(\text{transition metal cation Ni}^{2+}-\text{Co}^{2+}-\text{Mn}^{2+})=1.5:1$ of molar ratio. And a well-ordered layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powder is successfully synthesized by mixing uniform co-precipitation metal hydroxide $(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})(\text{OH})_2$ with 8% excess $\text{LiOH}\cdot\text{H}_2\text{O}$ under different calcinations temperatures. The XRD results show that the I_{003}/I_{104} values of all samples are larger than 1.2, which illustrates no undesirable cation mixing

to be occurred. The results of electrochemical properties experiments show that the ideal synthesizing conditions are $950\text{ }^\circ\text{C}$ for 10 h. The layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ material prepared under the optimal conditions has the I_{003}/I_{104} ratio of 1.26 and delivers the highest initial discharge capacity of $174.6\text{ mA}\cdot\text{h/g}$ ($2.8\text{--}4.5\text{ V}$, 16 mA/g), the smallest irreversible capacity loss of 9.7%, and the highest capacity retention of 95.4% after 50 cycles at 32 mA/g .

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