

## Synthesis of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode material by chloride co-precipitation method

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**Abstract:**  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  was prepared by a chloride co-precipitation method and characterized by thermogravimetric analysis, X-ray diffractometry with Rietveld refinement, electron scanning microscopy and electrochemical measurements. Effects of lithium ion content and sintering temperature on physical and electrochemical performance of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  were also investigated. The results show that the sample synthesized at 750 °C with 105% lithium content has fine particle sizes around 200 nm and homogenous sizes distribution. The initial discharge capacity for the powder is 184 mA·h/g between 2.7 and 4.3 V at 0.1C and room temperature.

**Key words:** lithium ion battery;  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ ; chloride co-precipitation; Rietveld refinement

### 1 Introduction

Recently, layered  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  has been intensively studied as a potential positive active electrode for application in batteries for hybrid electric vehicles (HEVs)[1–2]. It is reported that the mixed oxide inherits the merits of mono metal oxide such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$  and  $\text{LiMnO}_2$ , and exhibits high capacity, good cycling stability and excellent safety performance[3–6]. Nevertheless, compared with other lithium ion cathode materials, such as  $\text{LiFePO}_4$ , the cycling ability of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  still needs to be improved, due to irreversible capacity loss caused by cation mixing[2, 7–9]. Several effective ways have been proposed to lower the mixing degrees, including adding excess Li ion to restrain  $\text{Ni}^{2+}$  moved to Li layer, and substitution of a small quantity of layered metal by Al and Mg ions[2, 10–11].

The tradition way to synthesize  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  is co-precipitation method with sulphate and nitrate as raw materials, and their particle sizes are 10–40  $\mu\text{m}$ [9, 12]. As pointed out before, the electrochemical behavior of lithium ion cathode material is strongly influenced by preparation method, which includes different raw materials and particle size of final product[13–14]. It is also reported that submicron and nanometer particles are

conductive to shorten the Li ion diffusion route, and finally improve the electrochemical performance of material[15]. Therefore, we assumed that adding excessive Li and decreasing particle size maybe benefit the capacity and cycling-life of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ . In this work, through a chloride co-precipitation method, submicron  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  was attained, and effects of lithium ion content and sintering temperature on physical and electrochemical performance of final products were also investigated.

### 2 Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  was synthesized with the starting materials of  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ ,  $\text{NaOH}$  and  $\text{NH}_3\cdot\text{H}_2\text{O}$ .  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$  and  $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$  powders were dissolved in distilled water to obtain 2 mol/L solution ( $n(\text{Ni}):n(\text{Co}):n(\text{Mn})=8:1:1$ ). The mixtures were filled in beaker and heated at 50 °C in water bath kettle, then  $\text{NH}_3\cdot\text{H}_2\text{O}$  and 2 mol/L  $\text{NaOH}$  were added to the solution to control the pH value between 11 and 12. After being stirred for 5 min, the solution was filtered to separate the precipitate powders, and the powder was washed with distilled water and dried at 100 °C for 8 h. Later,  $\text{LiOH}$  was milled with the powder for 0.5 h in stoichiometric ratios of Li to (Ni+Co+Mn) is 1.03, 1.05

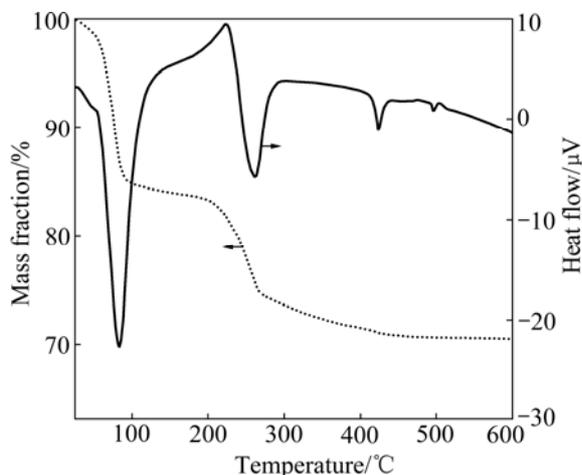
and 1.07, respectively, and the obtained mixture was sintered at 480 °C for 5 h, and then sintered at 750 °C for 12 h in O<sub>2</sub> atmosphere, respectively. After being cooled to room temperature, the final samples were obtained.

The TG—DTG analysis was tested by SDTQ600 with a step time of 10 (°)/min in O<sub>2</sub> atmosphere. The crystalline nature of the samples was identified with X-ray diffractometry (XRD, Dmax/2550VB+18 kW, Rigaku using monochromatic Cu K<sub>α</sub> radiation with a step time of 2(°)/min), and X-ray Rietveld refinement was performed by FULLPROF. Powder morphologies were observed by scanning electron microscope (SEM, JEOL JSM-5600LV).

The electrochemical properties of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> were measured by using 2025 button cell. The cathode consisted of 80% (mass fraction) active material, 10% acetylene black and 10% PVDF binder. A lithium metal foil was used as anode. LiPF<sub>6</sub> (1 mol/L) in a 1:1:1 (volume ratio) mixture of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC) was used as electrolyte. Charge-discharge performances were evaluated using a battery test system (BTS-5V/1mA, Xinwei 2.7–4.3 V).

### 3 Results and discussion

The TG—DTG curves of the mixture of LiOH·H<sub>2</sub>O and Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>(OH)<sub>2</sub> powders are shown in Fig.1. It is clear that three endothermic peaks and mass loss sections appear at 80–96 °C, 226–273 °C, 430 °C, respectively, which represent the loss of absorbed water, dehydration reactions of LiOH·H<sub>2</sub>O and Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>(OH)<sub>2</sub>, respectively. With the increase of temperature, the dehydration products, Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> and Li<sub>2</sub>O, react slowly to LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>. Owing to the fact that the reaction is composed by several sections including dehydration process as shown above, two-

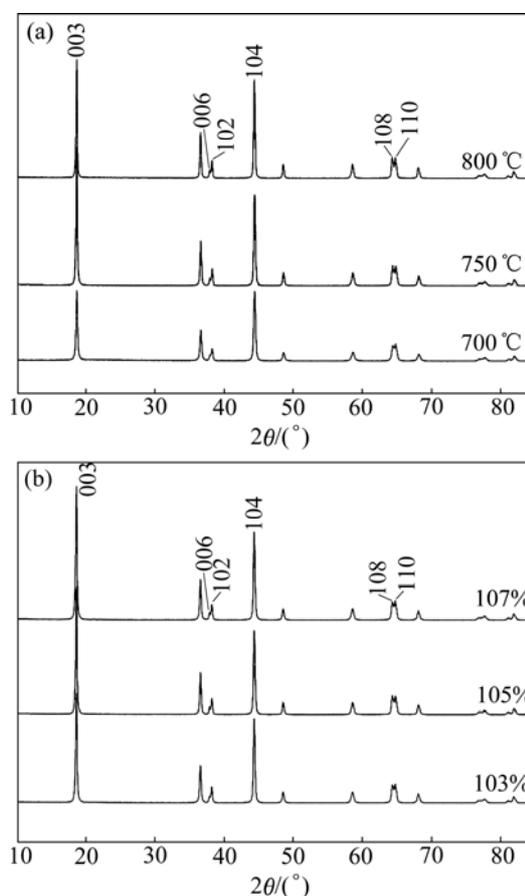


**Fig.1** TG—DTG curves of mixture of LiOH·H<sub>2</sub>O and Ni<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>(OH)<sub>2</sub> powders

section sinter should be introduced to ensure sufficient decomposition and contact between LiOH·H<sub>2</sub>O and precursor, and finally attain well electrochemical performance.

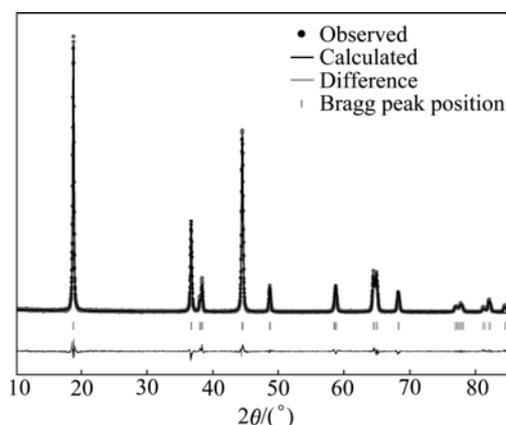
Fig.2 shows the XRD patterns of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>, synthesized at different temperatures or Li ion content. It is noted that all diffraction lines are indexed on the basis of the rhombohedral α-NaFeO<sub>2</sub> structure with a space group of R-3m. The samples with 105% Li ion content in Fig.2(a) were prepared at 700, 750 and 800 °C, respectively. It is obvious that the ratio of I<sub>003</sub> to I<sub>104</sub> for LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> powder obtained at 750 °C is 1.51, larger than 1.01 and 1.20 obtained at 700 °C and 800 °C, respectively, which scales lower mixing degree of Ni<sup>+</sup> in Li layer than others. As we know, the excess of Li<sup>+</sup>, whether in Li layer or in transition metal layer, will suppress the migration of Ni<sup>+</sup> into Li layer. Fig.2(b) shows the effect of various Li<sup>+</sup> contents on the XRD pattern of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> powders prepared at 750 °C. It is found that the ratio of I<sub>003</sub> to I<sub>104</sub> for LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> powders is gradually enhanced from 1.29, 1.51, to 1.52 with the increase of Li ion content.

The corresponding Rietveld refinement plot and parameters of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> powder synthesized at 750 °C are shown in Fig.3 and Table 1, respectively.



**Fig.2** XRD patterns of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>, synthesized at different temperatures (a) and Li ion contents (b)

The refinements were performed by assuming a partial occupation of Ni in the Li layers. The refinement results are in good agreement between the observed and calculated patterns in Fig.3 with high reliability factor. As seen in Table 1, only 5.5% Ni moves to the 3b-site (lithium site), and the lattice parameters of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  are smaller compared with the results from other research groups. WOO et al[11] reported that  $a=0.286\ 87\ \text{nm}$ ,  $c=1.425\ 31\ \text{nm}$ , which demonstrated that well-ordering layered and smaller  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  powder can be prepared by chloride co-precipitation method.



**Fig.3** Rietveld refinement patterns of XRD data for  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  (synthesized with 105% Li ion content at 750 °C)

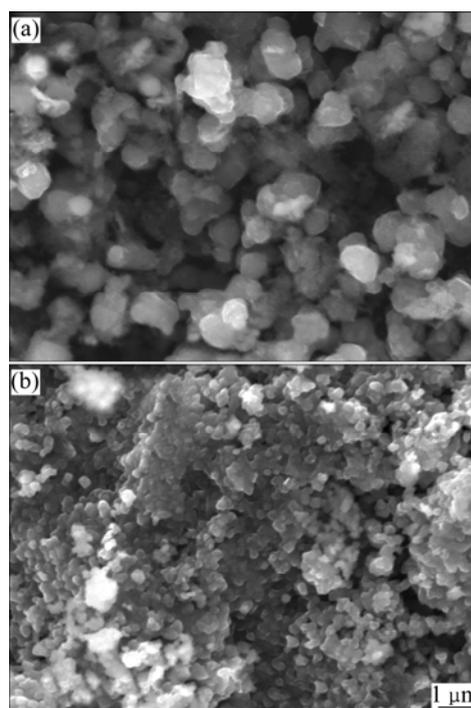
**Table 1** Structural parameters obtained from Rietveld Refinement of XRD data of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$

| Atom            | Site | x | y | z                | Occupancy |
|-----------------|------|---|---|------------------|-----------|
| Li <sub>1</sub> | 3b   | 0 | 0 | 1/2              | 0.945 (3) |
| Ni <sub>2</sub> | 3b   | 0 | 0 | 1/2              | 0.055 (3) |
| Ni <sub>1</sub> | 3a   | 0 | 0 | 0                | 0.749 (3) |
| Co <sub>1</sub> | 3a   | 0 | 0 | 0                | 0.102 (3) |
| Mn <sub>1</sub> | 3a   | 0 | 0 | 0                | 0.098 (3) |
| O               | 6c   | 0 | 0 | 0.259 22<br>(11) | 2.000     |

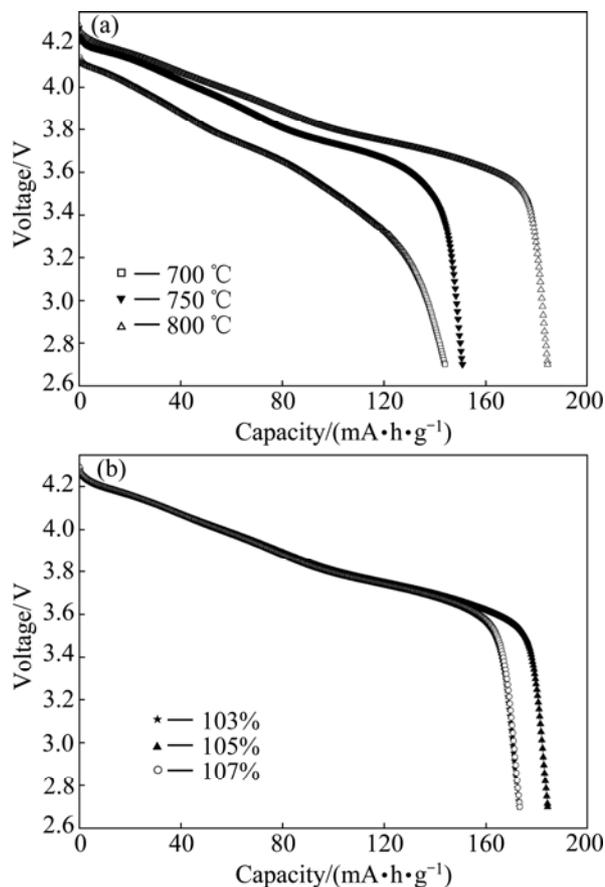
Note:  $a=b=0.286\ 588\ (4)\ \text{nm}$ ;  $c=1.419\ 938\ (5)\ \text{nm}$ ;  $R_p=7.09$ ;  $R_{wp}=8.8$ ;  $R_{exp}=1.85$ .

Fig.4 presents the SEM images of the precursor and  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  powder synthesized with 105% of Li content at 750 °C. As it can be seen that the particle morphologies of images are near-spherical and well distributed. And the particle sizes of precursor and  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  powders are fine, about 200 nm, which is conducive to shorten the lithium diffusion distance.

The initial discharge curves of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  prepared at different temperatures and Li ion contents are shown in Fig.5. The batteries were measured at about 10



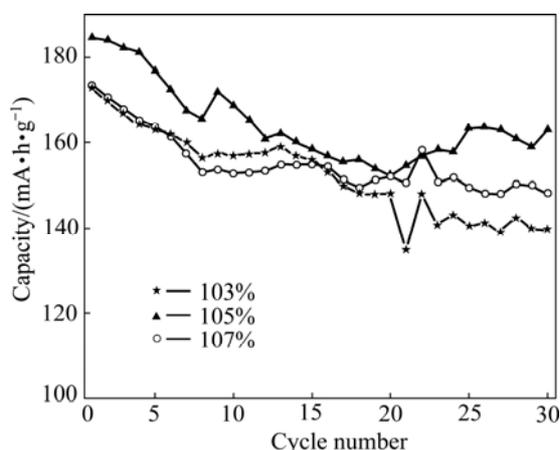
**Fig.4** SEM images of  $\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}(\text{OH})_2$  and  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$



**Fig.5** First discharge curves of  $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  synthesized at different temperatures (a) and Li ion contents (b) at 18 mA·h/g (0.1C) and 2.7–4.3 V

, 2.7–4.3 V and 0.1C (18 mA·h/g), respectively. All the samples exhibit a diagonal voltage plateau from 4.3 V to 3.58 V. In Fig.5, the sample obtained at 750 °C with 105% of Li ion content delivers the best discharge capacity, 184 mA·h/g, which is consistent with that shown in Fig.2 or Fig.3, that lower mixing degree of Ni<sup>2+</sup> in Li layer results in better electrochemical performance. It is also noted that the capacities of sample synthesized with 107% and 103% are almost equal, which can be ascribed that too much Li ion might occupy the site of transition metals, while, the lack of Li ion might induce to cation mixing, both of which should take responsibility to the capacity irreversible loss of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub>.

Fig.6 shows the cycling abilities of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> synthesized with different Li ion contents. After 30 cycles, all samples experience various capacity loss degrees. The sample prepared with 103% of Li ion content exhibits the worst cycle ability, and its discharge capacity was only 140 mA·h/g after 30 cycles. The capacity of sample prepared with 107% of Li ion content, on the other hand, exhibits 149 mA·h/g after 30 cycles. This demonstrated that excess Li ion can avoid cation mixing and improve cycle ability effectively. The sample prepared with 105% of Li ion content is found to be the optimum, which exhibited the highest discharge capacity and well cycle-life, with 169 mA·h/g after 30 cycles.



**Fig.6** Cycling performance of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> synthesized with various Li ion content tested at 0.1C and 2.7–4.3 V

## 4 Conclusions

1) Layered LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> compounds are synthesized with various Li ion contents at different temperatures by a chloride co-precipitation method.

2) XRD, Rietveld refinement and SEM analyses indicate that well-ordering, near-spherical and well distributed precursor has attained, and the particle size of

LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> compound is nearly 200 nm.

3) It is noted that the initial discharge capacity of the LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> synthesized with 105% of Li ion content at 750 °C is 184 mA·h/g, showing 169 mA·h/g after 30 cycles.

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