

Short communication

Studies on the low-heating solid-state reaction method to synthesize $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials

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Abstract

The low-heating solid-state method has been adopted to synthesize $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials. The final product, with homogeneous phase and smooth crystals indicated by XRD and SEM results, can be synthesized at 700°C , much lower than the synthesis temperatures of co-precipitation method. The reaction process and microstructure of precursor has been investigated by IR spectrum. By comparative studies with the mixture of CH_3COOLi and $(\text{Ni}, \text{Co}, \text{Mn})(\text{C}_2\text{O}_4)$, it is testified that the precursor is homogeneous, rather than a mixture. The decomposition process and the reaction energy have been studied to investigate the reaction mechanism of the precursor when heated at high temperature. The as-synthesized $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ exhibits excellent electrochemical properties, exhibiting initial specific capacity of 167 mAh g^{-1} with stable cyclic performance.

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Keywords: Low-heating solid-state reaction; $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$; Reaction energy; Cathode material; Lithium ion batteries

1. Introduction

It is of great importance to find out a high-efficiency and energy-saving synthesis method to replace the conventional chemical methods at present. Low-heating solid-state reaction is a synthesis method, which has been applied in the area of coordination, nano-materials and multi-metal oxides composite. It has been supposed as one of the most innovative methods to synthesize advanced materials due to its simplicity, low energy consuming and low cost. In the reaction, the crystal water was released during the mixing of raw materials, thus make the raw materials become a state of being melted. Therefore, the diffusion of molecules becomes easier and the reaction can be carried out at comparatively low temperatures.

Tang Research Group has been devoting great efforts in this field. They have synthesized a series of organic materials, and nano-materials. Besides, they have tried this method to synthesize cathode materials for lithium ion batteries, such as LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and LiMn_2O_4 [1–3]. However, the reaction mechanism of low-heating solid-state reaction is not very clear.

In this study, we adopted this method to synthesize the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials, which has been con-

sidered as the alternative material for commercial LiCoO_2 [4]. The reaction process and the structure of the precursor obtained by low-heating solid-state reaction have been studied. The synthesis kinetics of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials were studied by non-isothermal multiple-scan method with DSC at four heating rates. Additionally, the electrochemical properties of as-obtained $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ were investigated.

2. Experimental

Stoichiometric oxalic acid and $\text{LiOH}\cdot\text{H}_2\text{O}$ (molar ratio = 1:1) were ball milled for 2 h to make full reaction. The stoichiometric nickel acetate, cobalt acetate, and manganese acetate ($\text{Ni}:\text{Co}:\text{Mn} = 1:1:1$) were then added in, and the mixture was ball milled for another 6 h to obtain pink paste precursors. The precursors were dried in a vacuum oven at 150°C for 24 h. The dried precursors were heated at various temperature in air to obtain final $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders.

The reaction process and the molecule structure of the precursor were deduced by comparison of the infrared (IR) spectrums of precursor and the mixture of lithium acetate and the transition metal oxalates (FI-IR670, NEXUS). The synthesis kinetic of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials was studied by thermogravimetric analysis (TG) and differential scanning calorimeter (DSC) (STA409-QMS). Powder X-ray diffraction (XRD, Japan, Rigaku, D/max-A) employing $\text{Cu K}\alpha$ radiation was used to

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identify the crystalline phase of the prepared powders. The powders were observed using scanning electron microscope (Japan, Hitachi, S-3500N).

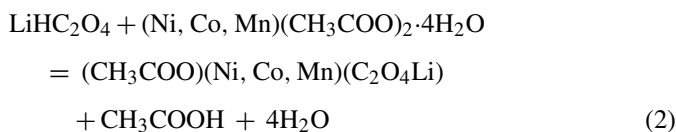
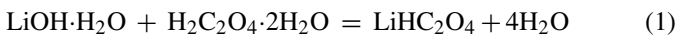
The positive electrode for the electrochemical studies was fabricated with: as-synthesized $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders, acetylene black as conducting additive, and teflon as binder in a weight ratio of 85:10:5. Testing cells were assembled and sealed in an Ar-filled glove box with the degreased electrode film as the cathode, lithium foil as the anode, 1 M LiPF_6 dissolved in EC/DMC/DEC (1:1:1 by mass) as the electrolyte and Celgard 2400 polyethylene/polypropylene as the separator. The cells were tested on a LAND BT-10 tester (Wuhan, China).

3. Results and discussion

3.1. The microstructure of the precursor

Firstly, we studied the reaction during the mixing of the raw materials. Fig. 1 shows the IR spectra of the precursors. The peaks at 3422 cm^{-1} , 1640 cm^{-1} and 619 cm^{-1} are assigned to absorbed water, and the twin peaks at 2362 cm^{-1} and 2345 cm^{-1} are assigned to CO_2 . Two weak peaks are observed at 2925 cm^{-1} and 2853 cm^{-1} , implying the presence of C–H stretching vibration. The several sharp peaks at 1631 cm^{-1} , 1419 cm^{-1} , 1318 cm^{-1} and 1027 cm^{-1} are assigned to COO^- . The peaks at $540\text{--}669\text{ cm}^{-1}$ are attributed to M–O bond.

According to the profile and other reports, the synthesis process is supposed to be



In order to testify that the precursor $(\text{CH}_3\text{COO})(\text{Ni, Co, Mn})(\text{C}_2\text{O}_4\text{Li})$ was obtained after the mixing of LiHC_2O_4 and $(\text{Ni, Co, Mn})(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, rather than a mixture of

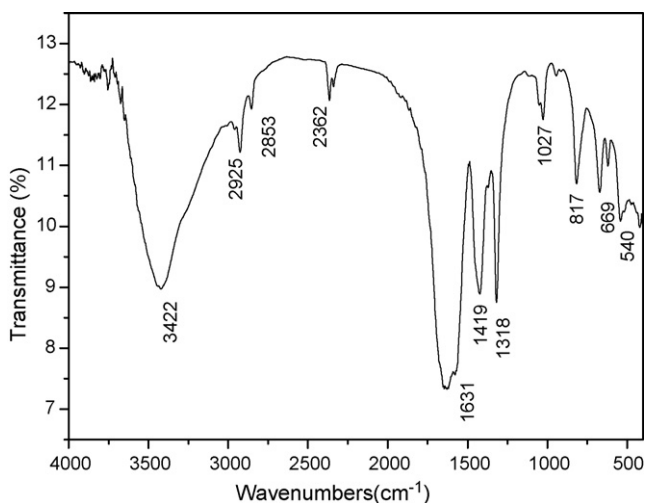


Fig. 1. IR spectrum of the as-synthesized precursors.

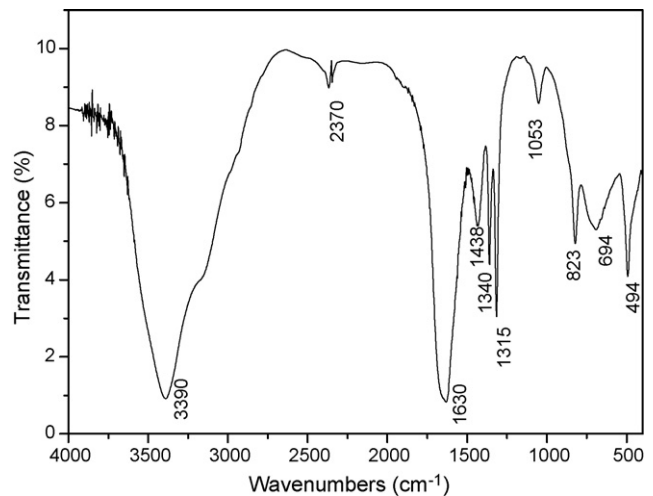


Fig. 2. IR spectrum of the mixture of CH_3COOLi and $(\text{Ni, Co, Mn})(\text{C}_2\text{O}_4)$.

CH_3COOLi and $(\text{Ni, Co, Mn})(\text{C}_2\text{O}_4)$, we also investigated the IR spectrum of CH_3COOLi and $(\text{Ni, Co, Mn})(\text{C}_2\text{O}_4)$ mixture. In Fig. 2, the apparent peak at 1340 cm^{-1} is caused by $-\text{CH}_3$ of CH_3COOLi . The peaks assigned to COO^- are not the same as those in Fig. 1, which means the microstructure of precursor is different from that of the mixture.

3.2. The decomposition of the precursor

The TG/DSC profiles for the mixed precursor of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials are shown in Fig. 3. The decomposition process of precursor is supposed to be divided into four stages (Table 1). The loss of weight from room temperature to $250\text{ }^\circ\text{C}$ can be assigned to the loss of absorbed water and methyl. The main exothermic peak at $300\text{ }^\circ\text{C}$ was associated with the decomposition and combustion of the constituents in the precursors. The minor weight loss between 300 and $400\text{ }^\circ\text{C}$ is due to the formation of final $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ powders. The overall weight loss of the TG curve is 57.2% , consistent with the value of weight loss in Table 1, which indicates the validity of the microstructure of the precursor and the synthesis reaction.

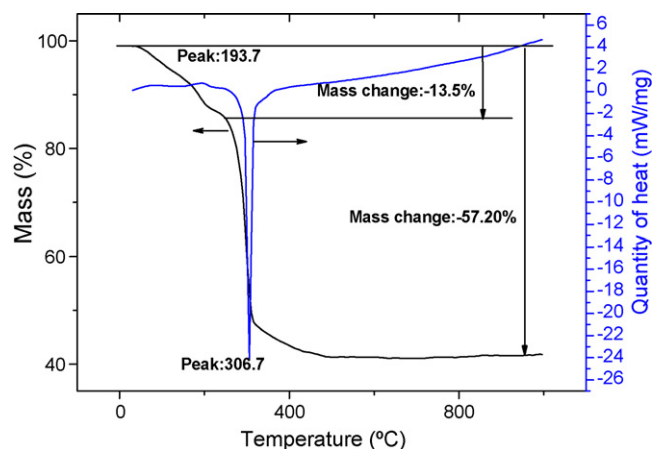


Fig. 3. TG/DSC profiles for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ precursor heat-treated from room temperature to $1000\text{ }^\circ\text{C}$ at $10\text{ }^\circ\text{C min}^{-1}$ in air.

Table 1
The decomposition process of the precursors according to the TG-DSC profiles

Stage	Endothermic/exothermic	Temperature (°C)	Reaction	Calculated weight loss (%)	Weight loss of TG curve (%)
I	Endothermic	150	The loss of absorbed water	7.8	6.0
II	Endothermic	193.7	The fracture of $-\text{CH}_3$	6.5	8.7
III	Exothermic	306.7	Fracture and oxidation of C–O	36.6	36.5
IV	–	–	Formation of LiMO_2 by Li–O and M–O	7	6.5

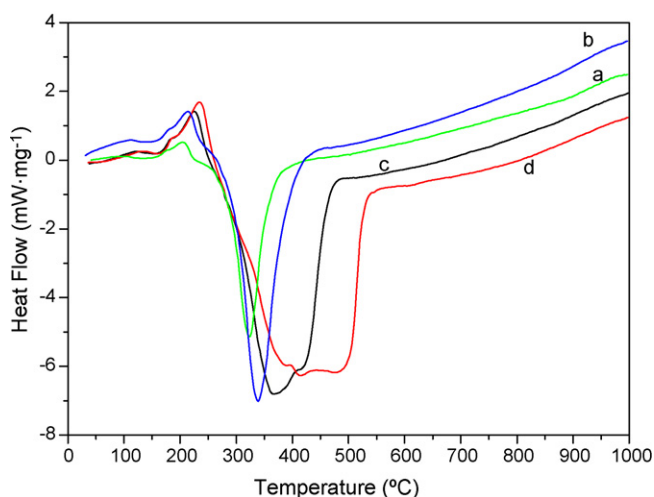


Fig. 4. DSC curves of the precursor heated in the range of room temperature to 1000 °C at four different rates: (a) 5 °C min⁻¹, (b) 10 °C min⁻¹, (c) 15 °C min⁻¹ and (d) 20 °C min⁻¹.

3.3. Reaction energy of the synthesis

The synthesis kinetics of layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials were studied by non-isothermal multiple-scan method with DSC at four heating rates (Fig. 4). We also calculated the reaction energy of the LiHC_2O_4 and $(\text{Ni, Co, Mn})(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ mixture as a comparison study of the obtained precursors

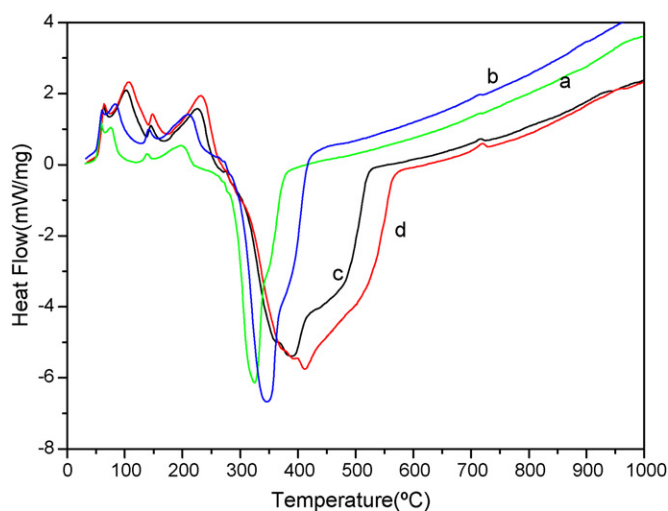


Fig. 5. DSC curves of CH_3COOLi and $(\text{Ni, Co, Mn})(\text{C}_2\text{O}_4)$ mixture heated between room temperature and 1000 °C at four different rates: (a) 5 °C min⁻¹, (b) 10 °C min⁻¹, (c) 15 °C min⁻¹ and (d) 20 °C min⁻¹.

(Fig. 5). In this paper, we applied two calculation models, one of which is Flynn–Wall–Ozawa method, an integral test, and the other is Kissinger method, the differential test [5]. For the Ozawa method, the calculation equation is

$$\log \beta = \log \frac{AE}{Rg(a)} - 2.315 - 0.4567 \frac{E}{RT} \quad (3)$$

The reaction energy can be calculated by slope of the $\log \beta \sim 1/T$ line. For the Kissinger method, the equation is

$$\ln \left(\frac{\beta}{T_p^2} \right) = \ln \frac{AR}{E} - \frac{E}{R T_p} \quad (4)$$

The reaction energy can be obtained by slope of the $\ln(\beta/T_p^2) - 1/T_p$ line.

The calculation result is shown in Table 2. The reaction energies of the precursors obtained by low-heating solid-state reaction are both lower than those of the mixture, which means that the precursor is easier to be decomposed at low temperature and synthesize the layered product. It is supposed that the metal ions were connected by the organic bonds, and after the decomposition of organic parts at low temperature, the ions can be easily combined to synthesize the layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$.

3.4. XRD and SEM of the obtained $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$

The XRD pattern of as-synthesized $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ in Fig. 6 indicates that the powders are well crystallized into single phase and the peaks can be indexed as the $R-3m$ space group. No traces of other phases appear in the XRD pattern. The lattice parameters of the sample were calculated by Rietveld refinement of the XRD pattern. The lattice parameters obtained are: $a = 2.857 \text{ \AA}$ and $c = 14.232 \text{ \AA}$, a little smaller than the values observed by Ohzuku ($a = 2.867 \text{ \AA}$, $c = 14.246 \text{ \AA}$). The ratio (R) of the lattice constants, c/a is 4.98 (>4.9), which reveals that the synthesized material has a well-defined layered structure. The clearly splits of $(006, 102)$ and $(108, 110)$ pairs in the XRD pattern also show the layered structure has been well formed.

Fig. 7 shows the morphology of synthesized $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ by heating the precursor at 700 °C

Table 2
The reaction energies of the precursors and the mixture by Ozawa and Kissinger methods

Methods	Ozawa	Kissinger
The precursor	27.9 kJ mol ⁻¹	18.3 kJ mol ⁻¹
The mixture	48.2 kJ mol ⁻¹	40.0 kJ mol ⁻¹

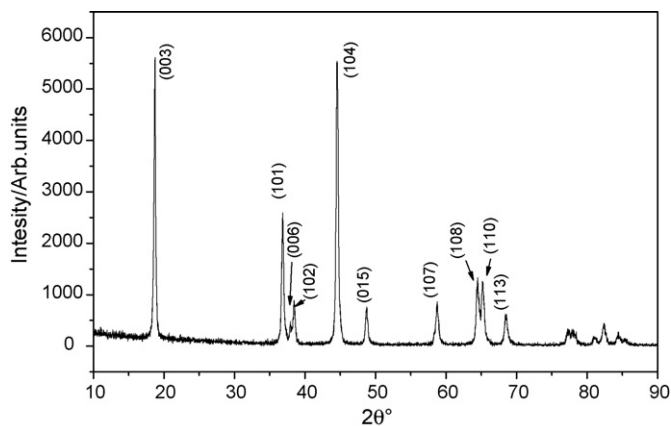


Fig. 6. XRD pattern of synthesized $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$.

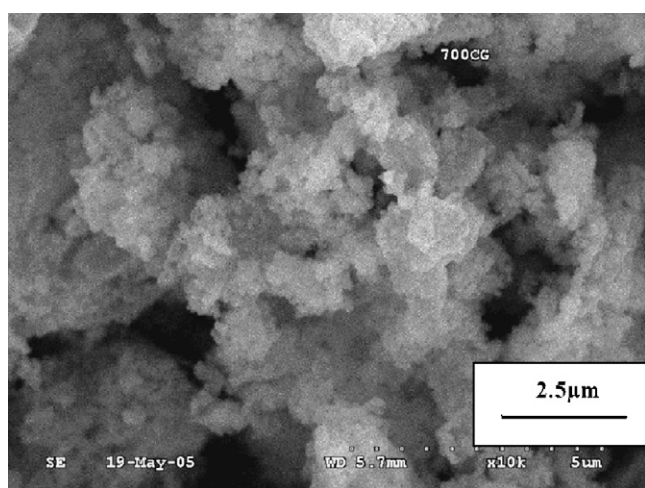


Fig. 7. SEM image of as-synthesized $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$.

for 15 h. It can be seen that the primary particles are all smooth and have uniform diameters ranging from 0.1 to 0.2 μm , which will enlarge the specific surface of the material, to improve the electrochemical properties of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$. The agglomerations will be beneficial to increase the tap density of as-synthesized materials.

3.5. Electrochemical characteristics of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$

Fig. 8 shows the charge/discharge performance of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ cell. The cell was charged at a constant current of 100 mA g^{-1} (0.5 C) in the voltage range of 2.7–4.35 V. The first charge/discharge specific capacity of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ at room temperature is 186/167 mAh g^{-1} . After 20 cycles, the cell showed little capacity loss, which indicated the excellent cyclic performance of the synthesized materials.

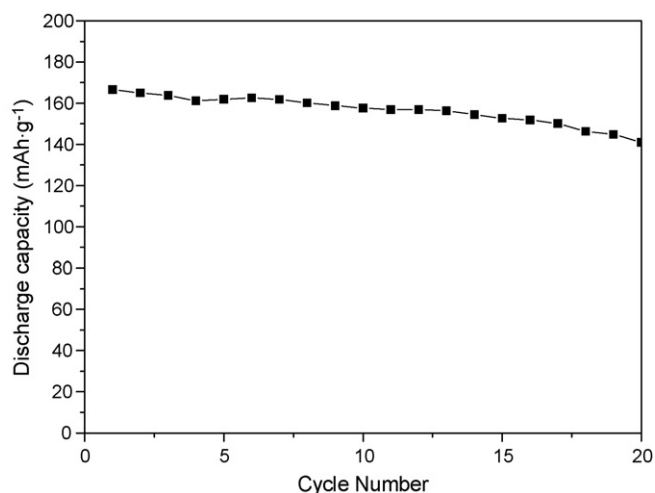


Fig. 8. Cyclic performances of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized at 700°C .

4. Conclusions

In this study, a new synthesis method, low-heating solid-state method, has been adopted to obtain $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ materials. The final product, with homogeneous phase and smooth crystals indicated by XRD and SEM results, can be synthesized at 700°C , at least 200°C lower than the synthesis temperature of liquid co-precipitation method. The reaction process and microstructure of precursor has been investigated by IR spectrum, compared with that of the mixture of CH_3COOLi and $(\text{Ni}, \text{Co}, \text{Mn})(\text{C}_2\text{O}_4)$. The decomposition process and the reaction energy have been studied to investigate the reaction mechanism of the precursor when heated at high temperature. It is deduced that the transition metal ions and lithium ions are connected together in the molecular of precursors by the organic group. Therefore, the reaction energy is decreased greatly. When heated, the organic parts are decomposed at comparatively low temperature and the final product is obtained. The as-synthesized $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ exhibits excellent electrochemical properties.

Acknowledgement

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