



# Facile synthesis of fusiform layered oxides assisted by microwave as cathode material for lithium-ion batteries



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## ABSTRACT

A facile microwave solvothermal reaction is performed to synthesize novel  $\text{LiMn}_{0.25}\text{Ni}_{0.5}\text{Co}_{0.25}\text{O}_2$  ternary layered oxide with 1 D fusiform morphology. Scanning electron microscopy (SEM) images show that material synthesized at  $800^\circ\text{C}$  well keeps the fusiform morphology of the precursor with a particle size of 100–300 nm. All the three elements are perfectly dispersed and a well-formed layered structure is obtained. Thus, good electrochemical performances with high initial discharge capacity of  $183\text{ mAh g}^{-1}$  is reached. Furthermore, high discharge capacity of  $154\text{ mAh g}^{-1}$  is remained with a capacity retention of 84.2% after 100 cycles at  $20\text{ mA g}^{-1}$ . Excellent rate capability is also obtained with high discharge capacity of  $99\text{ mAh g}^{-1}$  at  $2000\text{ mA g}^{-1}$ . It seems such facile microwave solvothermal method is one of the most promising candidates for preparing ternary layered oxides with excellent electrochemical properties as cathode material for lithium ion batteries.

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## 1. Introduction

Over the last decades, Lithium ion batteries (LIBs) have been significantly studied to realize the utilization of new energy [1,2]. Cathode material is considered as the most important part of LIBs and has undergone repeated reforms. Among various kinds of cathode materials, such as  $\text{LiCoO}_2$  [3],  $\text{LiFePO}_4$  [4–6],  $\text{LiMn}_2\text{O}_4$  [7,8] and so on, ternary layered oxide with similar structure as  $\text{LiCoO}_2$  which contains manganese, nickel and cobalt elements is one of the most attractive candidates as cathode material for LIBs [9–14]. It is reported that it can deliver high specific capacity above  $200\text{ mAh g}^{-1}$  at a large chemical window of 2.5–4.5 V at room temperature. The lower cost, higher energy density and better environmental benignity comparing to  $\text{LiCoO}_2$  make it to be the next generation of cathode material in practical application. However, the lack of the efficient method to synthesize ternary layered oxides under controllable technique results in the complexity of preparation [15–17]. Normal solid-state reactions will lead to serious agglomeration and thus the high electrochemical property LIBs application of ternary layered oxides is limited to a great extent.

Many different methods have been applied to obtain ternary layered oxides as cathode material for LIBs. Among them, co-precipitation method is the most widely used one and has already been commercially applied for production [18–21]. Spherical hierarchical morphology with primary particles can be obtained after long time co-precipitation. Thus, this method is very rigorous. Precise control of the pH value is necessary to obtain well-formed ternary oxides [18]. And it is also equipment and time cost. Usually, more than 10 h are necessary for the co-precipitation processes. In addition, there is space and time difference existing among the precipitation of Mn, Ni and Co ions [22]. In order to overcome some of the above disadvantages of the co-precipitation method, homogeneous solvo/hydrothermal method [23,24] is investigated. However, owing to the complex components of the ternary oxides, it is hard to mix the manganese, nickel and cobalt at an atomic level using still hydrothermal processes. And it is also time-consuming, 10 to 24 h are usually required to obtain the precursors of the ternary oxides through traditional solve/hydrothermal methods.

It is reported that a well controllable construction of cathode material will significantly enhance the electrochemical performances. Thus, electrode material with various structure and morphology, such as nano-sheets or nano-plates [25,26], microtubes or nano-rods [27–29], hollow or core-shell structure [30–32] and 3D mesoporous/macroporous network materials [33–36] have been elaborately constructed by different methods. Here, in this present work, a fast-facile microwave solvothermal synthesis is

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performed to obtain  $\text{LiMn}_{0.25}\text{Ni}_{0.5}\text{Co}_{0.25}\text{O}_2$  ternary oxides with a fusiform morphology followed by high temperature solid state reactions. Microwave can offer a rapid and uniform heating through the interaction between the material molecule and the radiation which enhances the whole reaction process. The formation process of the precursor is thus finished within only 30 min at 200 °C with the assistance of the microwave. The final fusiform ternary oxides can exhibit excellent electrochemical performances. It is revealed that such facile microwave hydrothermal synthesis is a promising way to efficiently form ternary precursors with special morphology within less time for application.

## 2. Experimental

In order to obtain the precursors of ternary layered oxide  $\text{LiMn}_{0.25}\text{Ni}_{0.5}\text{Co}_{0.25}\text{O}_2$ , stoichiometric amounts (total 10 mmol) of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  were added into 30 mL deionized water till to obtain a transparent solution with continually stirring. Then, 20 mmol dimethyl oxalate is dissolved in 20 mL ethylene glycol. After pulling both solutions into a microwave hydrothermal system (WX-6000) together, the temperature of the reaction was set as 200 °C and the time is 30 min. After fast reactions, the microwave hydrothermal system cooled down to room temperature, and the centrifugation is applied to get the precipitate. After drying the precipitate at 60 °C in a vacuum oven, stoichiometric amounts of  $\text{LiC}_2\text{O}_4$  (3% excess) were mixed with the precursors thoroughly. At last, the mixture was calcined at 800 °C and for 16 h in air to obtain the ternary layered oxides  $\text{LiMn}_{0.25}\text{Ni}_{0.5}\text{Co}_{0.25}\text{O}_2$ , which were named as LMNCO-800 and LMNCO-900 for short.

The phase of the ternary layered oxides is tested by X-ray diffractometry (XRD) at a scan rate of 4° per minute with  $\text{Cu K}\alpha$  radiation from 10° to 80° on an X-ray diffractometer (D/max-2200-PC). The thermal analysis (TG/DSC) of the reactions was performed on thermo gravimetric analyzer (TGA/SDTA851) and thermal analyzer (STA 449 F3). Field emission scanning electron microscopy (SEM, SIGMA, ZEISS microscope) is used to characterize the morphologies of the ternary layered oxides. And the surface area was carried out on Brunauer-emmett-teller (BET) surface area analyzer (ASAP 2020).

The working electrodes were prepared as our previous work did [22]. And the area mass loading of the layered oxides electrode is about  $3.1 \text{ mg cm}^{-2}$  for LMNCO-800 and LMNCO-900. The galvanostatic discharge/charge tests were tested on a LAND battery test system (Wuhan, China) at room temperature at the electrochemical window of 2.5–4.5 V. The test current densities were set from 20 to 2000  $\text{mA g}^{-1}$ . Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (CHI660E). The CV test was tested under the condition of the potential window of 2.5–5.0 V (vs.  $\text{Li}/\text{Li}^+$ ) and a scan rate of  $0.1 \text{ mV s}^{-1}$ . EIS test was carried out using a three-electrode cell using metallic lithium foil as both the counter and reference electrodes and the ternary layered oxides as the working electrode.

## 3. Results and discussion

### 3.1. Material characterization

TG and DSC test were first carried out to analyze the heat-treatment processes in  $\text{O}_2$ , as shown in Fig. 1. The faint mass change before 180 °C is attributed to the loss of surface water which is inevitable during the synthesis. The decomposing of the precursor happens from 180 °C with the appearance of the  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Thus, the mass of the sample decreases rapidly with a distinct

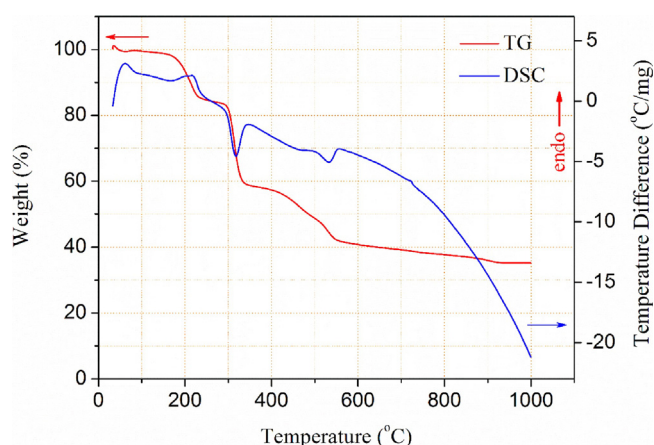


Fig. 1. TGA/DSC curves of mixture including the precursor and lithium resources.

exothermic peak in the DSC curve. Then, at about 400 °C, the oxidation of the transition metal element begins with a minor mass loss which is ascribed to the  $\text{O}_2$  absorption from the atmosphere. It reveals that the phase of the layered oxide begins to form above about 600 °C. Thus, 800 °C and 900 °C are chosen as the reaction temperature in this work to make sure a thoroughly formed layered structure with high crystallinity. XRD patterns of the as-prepared LMNCO-800 and LMNCO-900 are shown in Fig. 2. All the diffraction peaks for both samples could be indexed to as the structure of  $\alpha\text{-NaFeO}_2$  (hexagonal lattice, space group R-3m) [14]. There is not any impure phase appearing in the XRD patterns. Remarkable splitting of (006)/(012) and (108)/(110) peaks are observed for both LMNCO-800 and LMNCO-900, which indicates the formation of layered structure under the temperature of 800 °C and 900 °C [37–39]. Both patterns have small half widths which is ascribed to the good crystalline of the ternary layered oxides. XRD tests reveal that well-formed ternary layered oxides are obtained through our facile microwave hydrothermal synthesis followed by high temperature solid state reactions at 800 °C and 900 °C.

The SEM images of the ternary layered oxides after microwave hydrothermal reactions and synthesized at different temperatures are displayed in Fig. 3. Fig. 3(a) and (b) shows that the as-prepared precursors exhibit a fusiform morphology and a smooth surface, which means a good growth of the crystallite under the condition

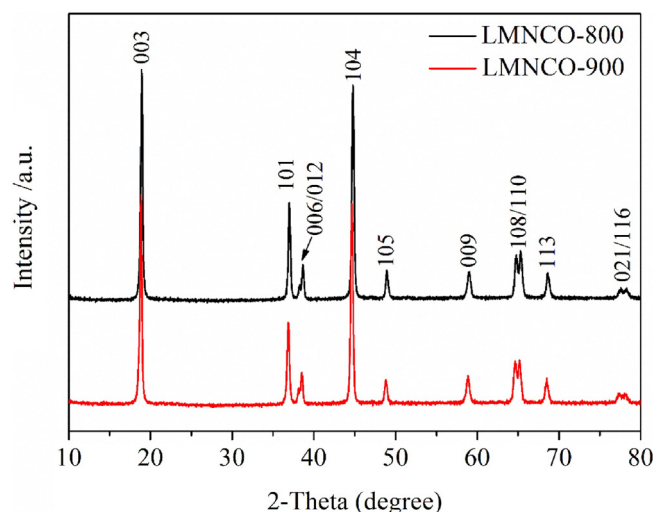


Fig. 2. XRD patterns of  $\text{LiMn}_{0.25}\text{Ni}_{0.5}\text{Co}_{0.25}\text{O}_2$  synthesized at 800 °C (LMNCO-800) and 900 °C (LMNCO-900).

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