

Short communication

Synthesis and electrochemical characterization of 5 V $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ cathode materials by low-heating solid-state reaction

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Abstract

$\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ as a 5 V cathode material, was prepared by low heating solid-state reaction with heating the mixed precursors at 500, 600, 700 °C. X-ray diffraction patterns of the prepared samples are identified as the spinel structure with a space group of $Fd\bar{3}m$. Scanning electron microscope was used to study the morphology of the synthesized $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ powders. The charge–discharge curves of the samples synthesized by low-heating solid-state reaction appear a plateau at 4.7 V.

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1. Introduction

Lithium-containing manganese oxides are the most promising cathode active materials for lithium secondary battery in terms of low cost, abundance, and non-toxicity [1–5]. However, there is a further demand for even higher specific energy density in the application of high power devices such as electric vehicles [6]. Many researchers have devoted much attention to the synthesis of advanced 5 V cathode materials based on the spinel $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ structure, which can provide much higher specific energy density with higher working voltages. These materials are substituted spinel compounds of the general formula of $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ with transition metal (Ni, Co, Cu, Cr, Ti, Al) [7]. $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ has a voltage plateau around 4.7 V versus Li metal, whose voltage is about 0.3 V, lower than that of the other 5 V cathode materials with spinel structure. In spite of the disadvantage, the spinel $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ has become the most interesting material for its structure stability, low electrolyte decomposition at high voltage and high theoretical capacity at 4.7 V region [6,8,9].

At present, the synthesis of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ is commonly adopting sol–gel synthesis method [10] which is preferable to form a stoichiometric proportion of multicomponent solid solution, or the high temperature solid state reaction [11] which

requires very high sintering temperature around 900 °C and long time with protective atmosphere.

Tang et al. [12] has prepared the cathode materials by low-heating solid-state reaction in which the starting materials form mixed precursors and the synthesis temperature is reduced. It has been confirmed that the low-heating solid-state synthesis is a simple and effective method to fabricate several chemical compounds [12,13].

In this study, $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ materials were prepared by low-heating solid state coordination method. The X-ray diffraction (XRD) and scanning electron microscope (SEM) were employed to obtain the structure information of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. The electrochemical kinetic properties were also studied.

2. Experimental

Stoichiometric oxalic acid and $\text{LiOH}\cdot\text{H}_2\text{O}$ (molar ratio, 1:1) were ball milled for 2 h in order to make them react fully. And then, stoichiometric nickel acetate and manganese acetate (Ni:Mn = 1:3) were 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 temperatures (500, 600, 700 °C) in air to obtain final $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ samples.

The thermal decomposition behaviors of the precursors were investigated by thermo gravimetric analysis (TG) and differential scanning calorimeter (DSC) at a heating rate of 10 °C min^{-1} .

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The prepared samples were characterized by powder X-ray diffraction (XRD, D/max-rb diffractometer, Rigaku, Japan) using Cu K α ($\lambda = 1.54056 \text{ \AA}$) radiation at room temperature. The scanning electron micrograph (SEM, S-3500N, Hitachi, Japan) was used to observe the particle morphology.

For electrochemical measurement, the electrode was prepared by rolling a mixture of 85% (mass fraction, so as the follows) active materials, 10% acetylene black and 5% polytetrafluoroethylene (PTFE). The electrodes were vacuum dried at 120 °C over 12 h, and then the testing cells were assembled in an argon filled glove box. Lithium metal was used as the counter electrode, porous polypropylene (celgard2300) as the separator. The electrolyte was 1.0 M LiPF₆ in a mixture of DMC, EC and DEC, 1:1:1 (v/v) (Li-battery grade, Samsung).

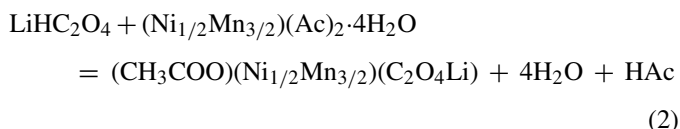
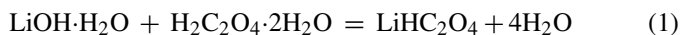
A computer controlled LAND BT1-10 8-channel battery cyler was used for half-cell cycle test. The cells were tested using constant current-charge and discharge in voltage range between 3.5 and 4.9 V. The current density was selected as 70 mA g⁻¹.

3. Results and discussion

3.1. Thermal properties

Fig. 1 shows the TG/DSC profiles for the mixed precursor, mainly composed of (CH₃COO)(Ni_{1/2}Mn_{3/2})(C₂O₄Li).

According to the TG-DSC profile and other reports [14,15], the synthesis process of precursors is supposed to be:



The loss of weight from room temperature to 200 °C can be assigned to the loss of absorbed water and the residual CH₃COOH. The weight loss between 200 and 310 °C is

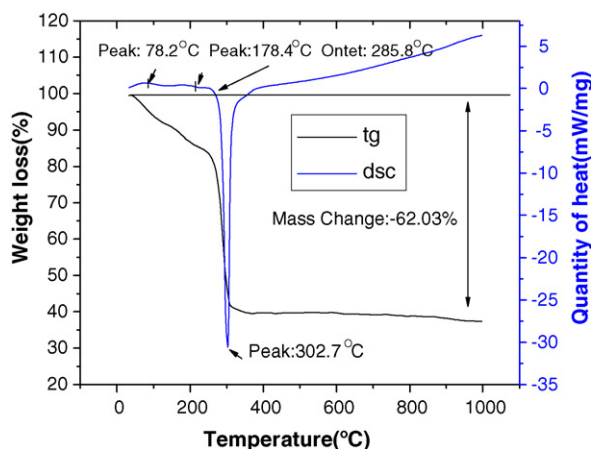


Fig. 1. TG/DSC profiles for LiNi_{1/2}Mn_{3/2}O₄ precursor heat-treated from room temperature to 1000 °C at 10 °C min⁻¹ in air.

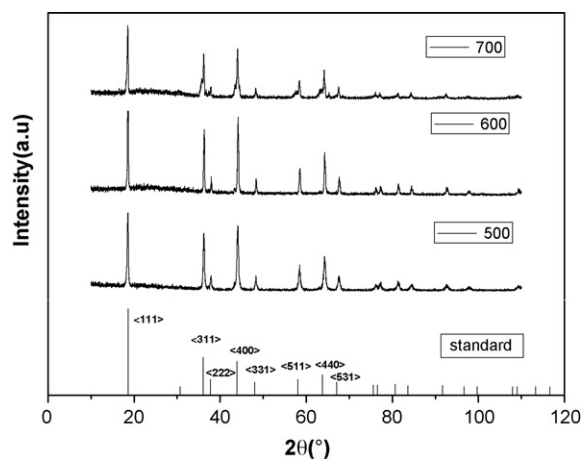


Fig. 2. XRD patterns of LiNi_{1/2}Mn_{3/2}O₄ heated at various temperatures (500, 600, 700 °C).

associated with the decomposition and combustion of the constituents in the precursors and due to the formation of final Li(Ni_{1/2}Mn_{3/2})O₄ powders, which corresponds to an exothermic peak on the DSC curve. The overall weight loss of the TG curve is consistent with the value of weight loss in experiments, which indicates the validity of the synthesis reaction. The weight remains unchanged above 400 °C, so 500, 600 and 700 °C are selected as the three synthesis temperatures.

3.2. Crystal structure properties

Fig. 2 shows the X-ray diffraction patterns of the final products synthesized at various temperatures (500, 600, 700 °C). All the peaks correspond to the spinel-type structure with space group of *Fd3m* based on standard LiMn₂O₄ structure [16]. No impurity phase is observed in the XRD patterns heated at different temperatures, which implies that even at the temperature of 500 °C, LiNi_{1/2}Mn_{3/2}O₄ powders will be synthesized.

3.3. Morphology of the synthesized LiNi_{1/2}Mn_{3/2}O₄ powders

The SEM images of LiNi_{1/2}Mn_{3/2}O₄ heated at different temperatures are given in Fig. 3. The powders of sample synthesized at 500 °C have uniform solid agglomerates with the particle size ranging from 0.25 to 0.5 μm. The particle size of the other two samples is nonuniform. The surfaces of the particles become smoother while the sizes become larger when heated at higher temperature.

3.4. Electrochemical properties

The cells were tested using constant current-charge and discharge between 3.5 and 4.9 V. The current density was selected as 70 mA g⁻¹. Fig. 4 shows the charge–discharge curves of the synthesized samples. It is clear that the samples show high voltage plateau around 4.7 V versus Li metal. So the 5 V cathode materials LiNi_{1/2}Mn_{3/2}O₄ was successfully synthesized by low heating solid-state reaction at 500, 600 and 700 °C.

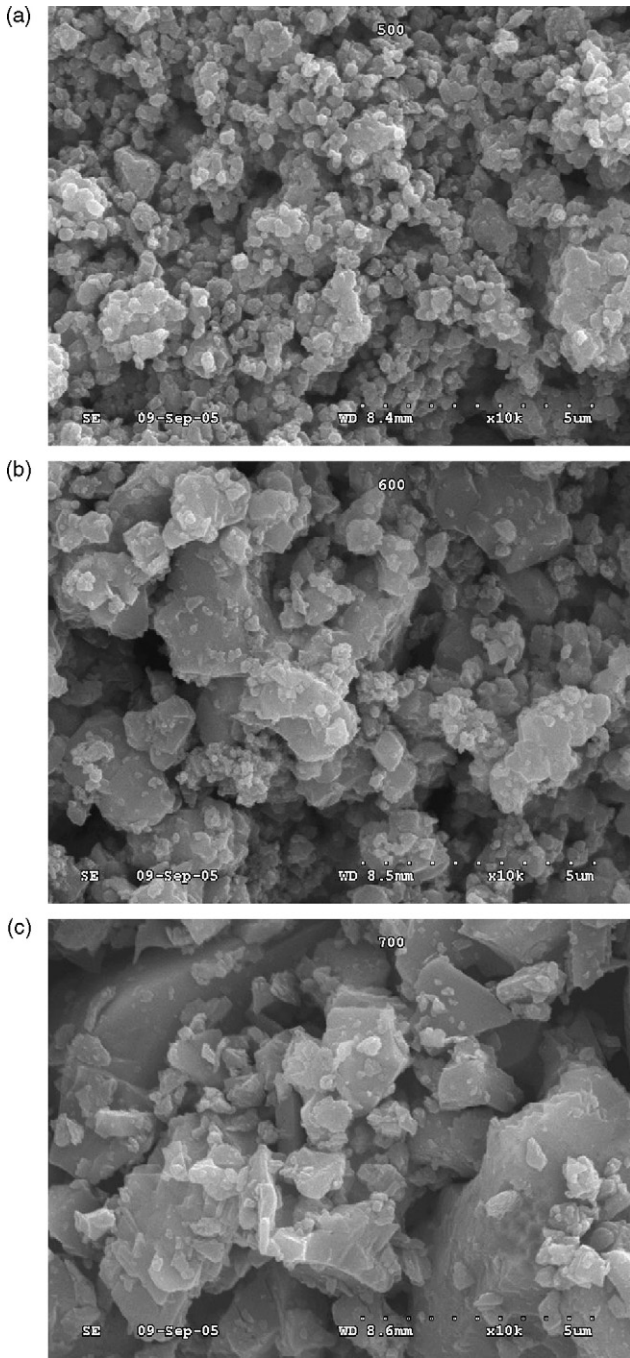


Fig. 3. SEM images of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ synthesized at 500 °C (a), 600 °C (b) and 700 °C (c).

Fig. 5 shows the cycling performance of the samples prepared at different temperatures. The first discharge specific capacities of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ at room temperature are 102, 112, and 88 mA h g^{-1} for samples heated at 500, 600, 700 °C, respectively. The reversible capacities after 20 cycles are 117 mA h g^{-1} (114% of the first discharge capacity), 110 mA h g^{-1} (98.2% of the first discharge capacity), and 110 mA h g^{-1} (125% of the first discharge capacity) for samples synthesized at 500, 600, 700 °C, respectively. The reversible capacities of the samples synthesized at 500 and 700 °C increase with cycling except for a little decrease of the 600 °C heated sample. Fur-

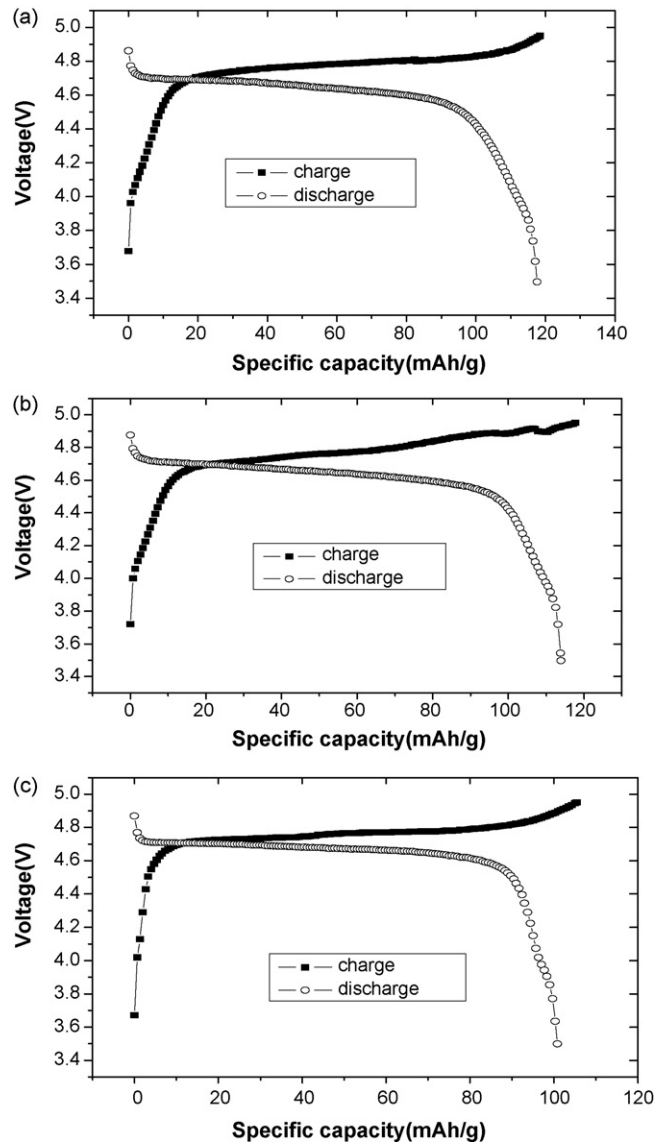


Fig. 4. Charge–discharge curves at the fourth cycle of the samples prepared with different calcinations temperature.

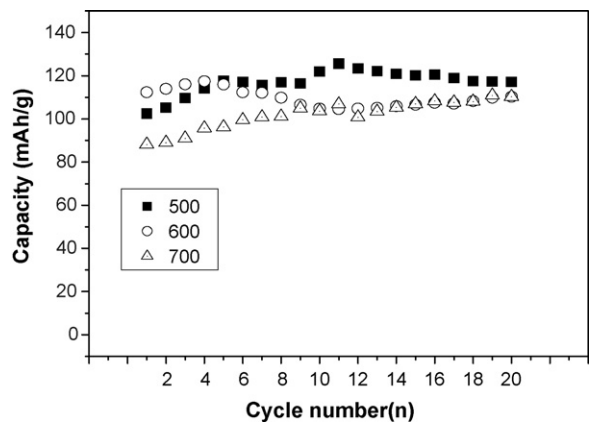


Fig. 5. Cycling performance of the samples prepared with different calcinations temperature.

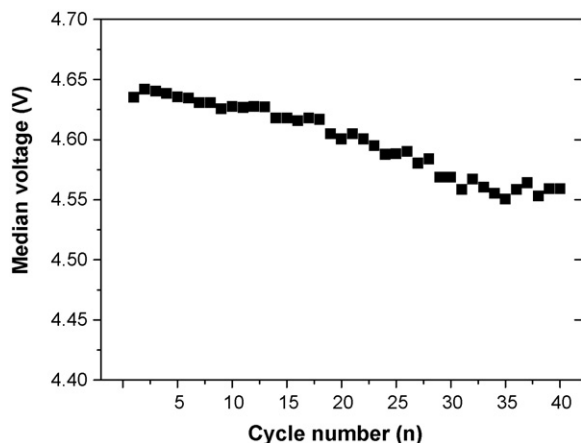


Fig. 6. The median voltage vs. cycle number of the sample prepared at 500 °C.

ther researches are certainly necessary to study the phenomena.

Fig. 6 shows the median voltage versus cycle number of the 500 °C synthesized sample. The median voltage of the sample decreases from 4.64 to 4.6 V in the first 20 cycles and to 4.56 V after another 20 cycles. The decrease of the median voltage with cycling is related to the structure of the $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ sample. The structure of the sample may change with cycling, and then the capacity at 4 V plateau increases. That interprets why the capacity of sample increases with cycling. Further researches will be done to investigate the structure change with cycling.

4. Conclusions

The 5 V cathode materials $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ were synthesized by low-heating solid-state reaction with heating the mixed precursors at 500, 600, 700 °C. The low-heating solid-state reaction, as an ideal method used to produce fine, chemically homogeneous and pure single phase powders, can solve the problem of the sol-gel synthesis method which is complicated, or the high temperature solid state reaction which requires very high sintering temperature and long time with protective atmosphere.

The XRD peaks correspond to the spinel-type structure with space group $Fd\bar{3}m$. The powders of the 500 °C synthesized sample have uniform solid agglomerates and the particle size ranges from 0.25 to 0.5 μm . The size of the other two samples is nonuniform. The surfaces of the particles become smoother while the sizes become larger when heated at higher temperature. During the electrochemical cycling, it is clear that the samples show high voltage plateau around 4.7 V versus Li metal and the capacity increases. But the median voltage decreased, which related to the structure change of the $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ sample. Further researches are needed to study the electrochemical properties of $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$ material.

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