Effect of Lithium Source on the Electrochemical Performance of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Synthesized by High Temperature Ball Milling Method

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ABSTRACT

LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ cathode materials were synthesized by the high temperature method under the same process conditions using different lithium source (LiOH, Li$_2$CO$_3$). The structure and morphology of synthesized powders were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) methods, and the electrochemical performance of the material was investigated by measurements of charge and discharge. The results showed that the synthesized LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ using Li$_2$CO$_3$ as the lithium source has a high electrochemical reversed. The specific discharge capacity is 155.7mAh/g under the discharge at 0.1C-rate, with a capacity retention rate of 99.7% over 25 cycles. So it has the excellent electrochemical performance.

INTRODUCTION

Lithium ion battery is recognized as "green power", because of its high specific capacity, long cycle life, high working voltage, good safety performance, low self-discharge, non-memory effect, no pollution-free and so on [1]. The three-element cathode material which was first reported by Ohzuku and Tsutomu [2] has attracted much attention. It includes all
advantages of lithium cobalt oxide, lithium manganese oxide and lithium nickel oxide respectively.

In recent years, more and more methods have been invented to synthesize the three-element cathode material. Such as co-precipitation method [3-5], solid phase method [6-8], sol-gel method [9, 10], microemulsion method [11], microwave method [12], spray drying [13] and combustion method [14].

In this work, LiNi1/3Co1/3Mn1/3O2 particles were synthesized by high temperature ball milling method which is a novel approach [15-17]. Aiming at the preparation of LiNi1/3Co1/3Mn1/3O2 particles with good electrochemical performance, different water-soluble lithium source were used as raw materials, and synthesized ball-milling temperature at 750 °C for 10h.

EXPERIMENTAL

Stoichiometric amounts of lithium source (LiOH, Li2CO3), NiO, Co3O4 and MnO2 were dissolved in boiling deionized water, and mixed with Li:Ni:Co:Mn molar ratio of about 3.09:1:1:1. They were then stirred by the stirrer. After stirring for two hours, they were oven-dried at 130°C. We obtained precursors which were placed in a high temperature ball milling equipment at a ball: weight ratio 15:1 and the synthesis process was conducted with different ball-milling temperatures 750°C reaction times for 12h, the process was conducted under an air atmosphere. Then the powders were obtained. The structure of the particle was characterized by Rigaku D/max-RB diffractometer type X-ray diffraction (XRD). The morphology and microstructure of LiNi1/3Co1/3Mn1/3O2 powders were characterized by Scanning electron microscopy (SEM HITACHI S-3000H).

The electrochemical properties of LiNi1/3Co1/3Mn1/3O2 powders were investigated using a two-electrode coin cell (CR2032) which the counter electrode is lithium metal. The separator was a porous polypropylene membrane (Celgard 2400). 1M LiPF6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) were used as liquid electrolyte. LiNi1/3Co1/3Mn1/3O2 powder, acetylene black, and polyvinylidene fluoride (PVDF) weight ratio of 80:10:10, respectively. They were weighted and mixed followed by adding some N-methyl pyrrolidone (NMP), then electrode slurry was obtained. The electrode slurry was coated on an aluminum foil and then was roasted at 120°C for 12 h. The cells were assembled in a glove box. The cycle charge-discharge test for button battery product at 0.1C-rate was conducted by Neware testing system from 2.5 to 4.3V at the room temperature (the current of 1 C equals to 200mA/g).
RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of LiNi1/3Co1/3Mn1/3O2 particles. The samples of LiNi1/3Co1/3Mn1/3O2 were synthesized with LiOH and Li2CO3 as lithium source. All diffraction peaks of the samples in XRD patterns clearly show a single phase formation of an α-layered structure without any impurity phase. LiNi1/3Co1/3Mn1/3O2 was synthesized with Li2CO3 as lithium source had higher diffraction peaks.

Fig. 2 shows the SEM images of LiNi1/3Co1/3Mn1/3O2 particles. When LiNi1/3Co1/3Mn1/3O2 obtained with LiOH as lithium source, which is the smallest but the severe agglomeration of particles occurs. However, when LiNi1/3Co1/3Mn1/3O2 obtained with Li2CO3 as lithium source, the size of the particles is obtained was homogeneously distributed, about 2 μm in diameter and 4μm in length.

Figure 1. XRD patterns of LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 particles obtained with different lithium source.

Figure 2. SEM images of LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 particles obtained with different lithium source : (a) LiOH, (b) Li_2CO_3.
Fig. 3 shows the influence of lithium source on the specific capacity of \( \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) between 2.5 and 4.3 V using a low current density of 0.1C-rate at room temperature. The initial discharge capacities of samples are 149.2 and 155.7mAh/g. When \( \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) obtained with \( \text{Li}_2\text{CO}_3 \) as lithium source, the sample has higher capacity.

Fig. 4 shows the cyclic performance of sample which synthesized with different lithium source at the current of 0.1C. It shows that the capacity of \( \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) sample synthesized with \( \text{LiOH} \) as lithium source was 142.9mAh/g, with a capacity retention rate of 95.8% over 25 cycles. The capacity of \( \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) sample synthesized with \( \text{Li}_2\text{CO}_3 \) as lithium source was 155.2mAh/g, with a capacity retention rate of 99.7% over 25 cycles, shows an excellent rate cyclic performance.

All the above results revealed that \( \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \) synthesized with \( \text{Li}_2\text{CO}_3 \) as lithium source had a single phase formation, a distributed uniformly small size and an excellent electrochemical performance. The reason for this is that \( \text{CO}_2 \) was generated when \( \text{Li}_2\text{CO}_3 \) decomposed. \( \text{CO}_2 \) may prevent the undesirable particle growth during the preparation of \( \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2 \).
CONCLUSIONS

In conclusion, LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ particles were synthesized by high temperature ball milling method. The effects of lithium source on the performance of the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ were investigated. Results showed that the product with Li$_2$CO$_3$ as lithium source synthesized ball-milling temperature at 750 °C for 10 h at a ball: weight ratio of 15:1, of which the initial discharge capacity is 155.7 mAh/g at 0.1C-rate. After 25 cycles, the capacity is 155.2mAh/g, with a capacity retention rate of 99.7%.

ACKNOWLEDGEMENTS

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

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