Int. J. Electrochem. Sci., 12 **(2017)** 7166 – 7173, doi: 10.20964/2017.08.42

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Effects of Sintering Time on the Performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Synthesized by High Temperature Ball Milling Method

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Received: 2 May 2017 / *Accepted:* 11 June 2017 / *Published:* 12 July 2017

Composite material $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode material for lithium-ion battery was obtained with lithium carbonate, nickel (II) oxide, cobalt (II, III) oxide and manganese dioxide as raw materials by high temperature ball milling method. To synthesis the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with excellent electrical properties, influence of ball-milling time was analyzed in this paper. Results showed that the best electrochemical performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was obtained from the test, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles acquired ball-milling temperature at 750℃ for 15h, and got performance uniformity of the material. Its initial discharge specific capacity reached 166.6 mAh/g at 0.1 C. The capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ sample was 157.5 mAh/g, with a capacity retention rate of 94.5% over 50 cycles.

Keywords: Composite materials; $LiNi1_{/3}Co_{1/3}Mn_{1/3}O_2$; High temperature ball milling method; Electrical properties; Ball-milling time

1. INTRODUCTION

The prospect of lithium-ion battery applications is very positive because of its high ratio of performance to price. Cathode material is an important part of the battery. The three-element cathode material which was first reported by Ohzuku and Tsutomu [1] is a new type of lithium ion batteries, which has the α-layered structure and high theoretical capacity of 278mAh/g. It includes all advantages of lithium cobalt oxide, lithium manganese oxide and lithium nickel oxide, respectively [2]. In the recent years, a lot of researches have been done on the development of the three-element cathode material, such as $LiNi_{0.4}Co_{0.2}Mn_{0.4}O_2$, $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ [3-6] and $LiNi_{0.475}Co_{0.05}Mn_{0.475}O_2$, especially for $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ [7, 8].

The three-element cathode material Lithium titan ate is generally synthesized by co-precipitation method [9-11], solid phase method [12-14], sol-gel method [15-17], microemulsion method [18], microwave method [19], spray drying [20] and combustion method [21]. The traditional high temperature solid-state synthesis method and liquid phase synthesis methods need extremely long synthesis time and a high-temperature calculation, and the latter needs a complex operation, organic reagents and a sophisticated apparatus. Recently, high-temperature ball milling method was reported. It applies to the ball-milling and sintering steps throughout the synthesis process, and was performed on a patented high-temperature ball-mill. The equipment was modified from a traditional mechanical ball-mill by adding a controllable heating device. Therefore, ball-milling and high-temperature heating occurs simultaneously throughout the process [22-24].

In this paper, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles were manufactured from Li_2CO_3, NiO, Co_3O_4 and MnO_2 by high temperature ball milling method. Aiming at the preparation of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles with good electrochemical performance, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles in different ball-milling time were synthesized by the high temperature ball milling method in order to investigate the effect of ball-milling time.

2. EXPERIMENTAL

Stoichiometric amounts of Li_2CO_3, NiO, Co_3O_4 and MnO_2 with Li: Ni: Co: Mn molar ratio of about 3.09:1:1:1 were dissolved in deionized water, they were then stirred by the stirrer. After stirring for two hours, they were oven-dried at 130℃. After the oven-dried processing, we obtained precursor particles. Then we put the precursor in the high temperature ball milling equipment (illustrated in Fig. 1) at a ball: weight ratio 15:1 [24] and the synthesis process was conducted ball-milling temperatures at 750℃ reaction different time (9, 12, 15 and 18h), the process was conducted under an air atmosphere. Then the powders were obtained.

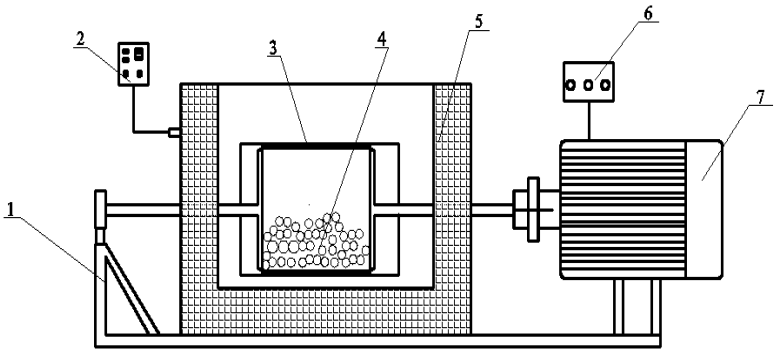

Figure 2. Illustration of the high temperature ball mill used in the study. 1-support base; 2-temperature controller; 3- ball milling canister; 4-grinding ball; 5-furnace body; 6-speed regulator; 7-electrical motor

The structure of the particle was characterized by Rigaku D/max-RB diffractometer type X-ray diffraction (XRD). The morphology and microstructure of $LiNi1_{/3}Co_{1/3}Mn_{1/3}O_2$ powders were characterized by Scanning electron microscopy (SEM HITACHI S-3000H).

The electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were investigated using CR2032 cell, which lithium metal as the counter electrode. The separator was a porous polypropylene membrane (Celgard 2400). 1M $LiPF_6$ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) were used as liquid electrolyte. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powder (80wt %), acetylene black (10wt %), and polyvinylidene fluoride (PVDF) (10wt %) 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℃ 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).

3. RESULTS AND DISCUSSION

The effects of ball-milling time on the crystal growth of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in the synthesis process were investigated. Fig. 2 shows the XRD patterns of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles. The samples of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were synthesized ball-milling temperature at 750℃ for 9, 12, 15 and 18h, respectively. All diffraction peaks of the samples in XRD patterns clearly show a single phase formation of an α-layered structure without any impurity phase, the crystallinity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples has minor increase with ball-milling time prolonging.

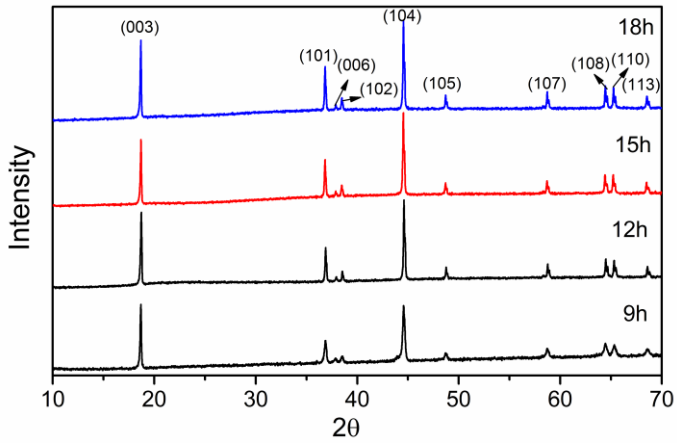

Figure 2. XRD patterns of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles obtained with different ball-milling time

Fig. 3 shows the SEM images of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles. The particles were reacted ball-milling temperature at 750℃ for 9, 12, 15 and 18h, respectively. SEM images show that the samples all contain similar small particles. When the ball-milling time was 9h, which is the smallest but severe agglomeration of particles occurs. When the ball-milling time were12, 15h, the particles were about

1μm in diameter and 3μm in length. However, the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles obtained in 15h were spherical shaped and homogeneously distributed, and the size of the particles were about 2 μm in diameter and 4μm in length. When ball-milling time increased to 18h, the grain sizes of the products notably increased and have the crystal agglomeration.

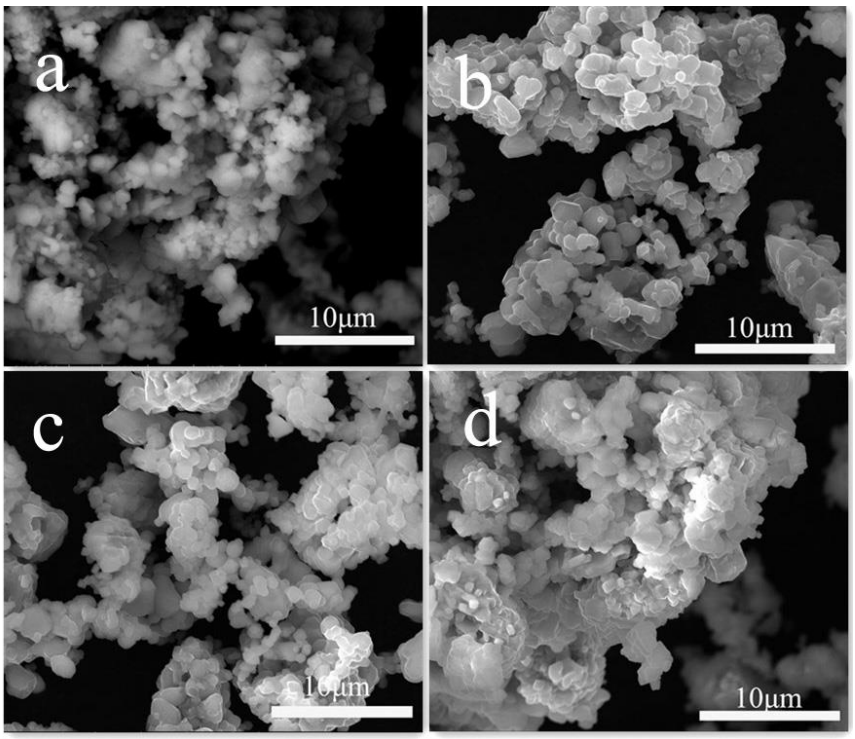

Figure 3. SEM images of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles obtained with different ball-milling time :(a) 9h, (b) 12h, (c) 15h, and (d) 18h

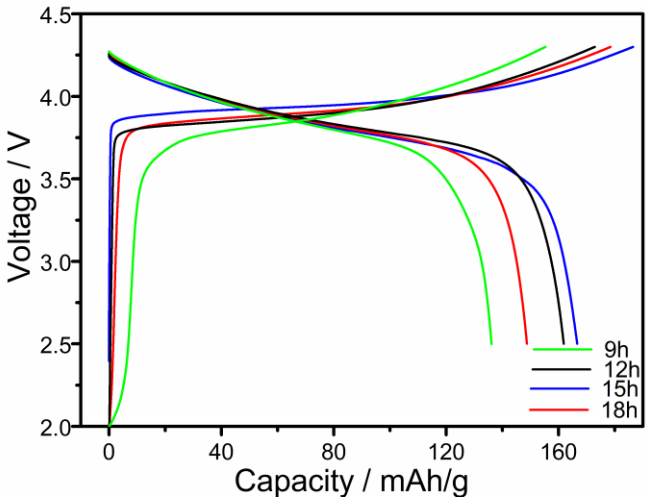

Figure 4. Charge/discharge curves of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles obtained with different ball-milling time

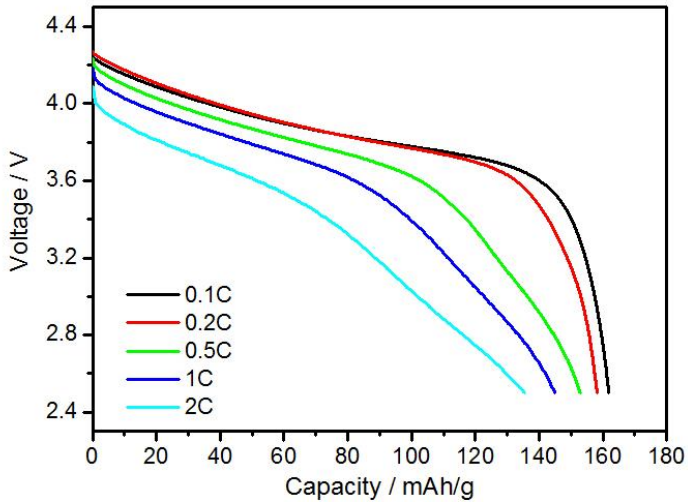

Figure 5. The initial discharge curves at various currents of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles obtained with ball-milling temperature 750℃for 15h

Fig.4 shows the influence of ball-milling time on the specific capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ 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 136.1, 161.8, 166.6 and 148.7mAh/g, respectively. When synthesized ball-milling time was 15 h, the sample has higher capacity than others.

Fig.5 shows the rate performance of the optimized sample of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles obtained with ball-milling temperature 750℃ for 15 h at various currents. At rates of 0.1, 0.2, 0.5, 1.0 and 2.0 C, the initial discharge capacities are 166.6, 158.1, 152.9, 144.9 and 135.3 mAh/g, respectively. The initial discharge capacities of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ were reduced little with the rise of current. The initial discharge capacity is 135.3 mAh/g at 2.0C-rate. It means $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ which synthesized ball-milling temperature at 750℃ for 15 h has an excellent low rate performance.

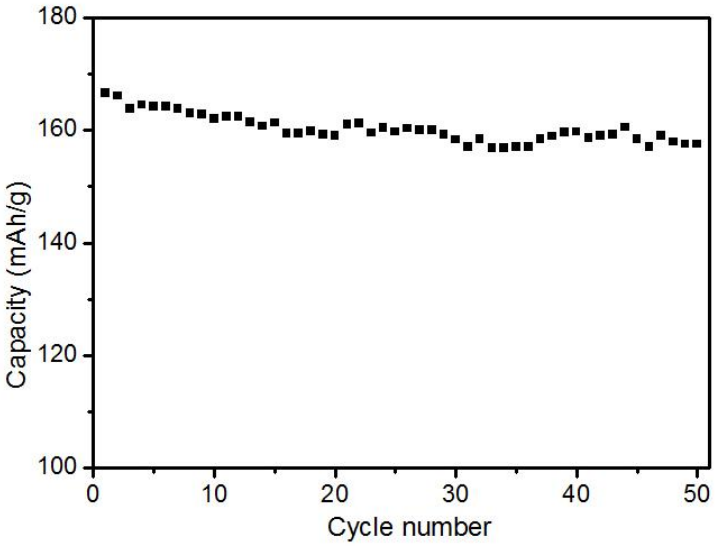

Figure 6. The cyclic performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles obtained with ball-milling temperature 750℃for 15h at 0.1C-rate

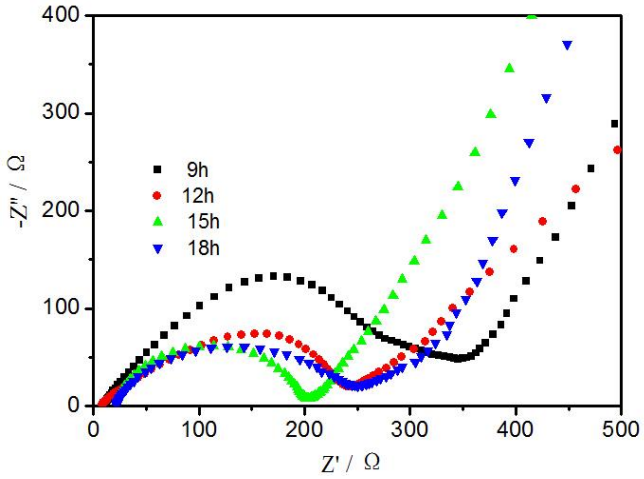

Figure 7. The Nyquist plots of $LiFePO_4$/C samples obtained with the different synthesis methods

The cycling performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrode which synthesized ball-milling temperature at 750℃for 15h was evaluated at the current of 0.1C, and the result is shown in Fig. 6. As shown in Fig.6, the capacity of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ sample was 157.5 mAh/g, with a capacity retention rate of 94.5% over 50 cycles. It shows an excellent rate cyclic performance.

Table 1. Comparison of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders on their electrochemical properties.

component	*Synthesizing method*	*Raw materials*	*Electrochemical performance*	*References*
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	High temperature ball milling method	Li_2CO_3 NiO Co_3O_4 MnO_2	167;0.1C (2.5-4.3)	As prepared
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Co-precipitation method	$NiSO_4{\cdot}6H_2O$ $CoSO_4{\cdot}7H_2O$ $MnSO_4{\cdot}H_2O$ $LiOH{\cdot}H_2O$	155; 0.5C (2.7-4.3)	[25]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Electrospinning	$LiNO_3$ $Ni(NO_3)_2{\cdot}6H_2O$ $Co(NO_3)_2{\cdot}6H_2O$ $Mn(NO_3)_2{\cdot}6H_2O$	139;0.5 C (3-4.5)	[26]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Original wet-chemical route	$Ni_{1/3}Co_{1/3}Mn_{1/3}(OH)_2$ $LiOH{\cdot}H_2O$	150;0.5 C (3.0-4.3)	[27]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Microwave-hydrothermal method	$Ni(NO_3)_2$ $Co(NO_3)_2$ $Mn(NO_3)_2$ $LiOH{\cdot}H_2O$	160; 0.1C (2.7-4.3)	[28]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Solid-state method	$LiOH{\cdot}H_2O$ $Ni(OH)_2$ Co_2O_3 MnO_2	155; 0.1C (3.0-4.3)	[28]
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Rheological phase method	$LiOH{\cdot}H_2O$ $Ni(OH)_2$ Co_2O_3 MnO_2	167; 0.1C (3.0-4.3)	[29]

EIS was also employed to study the prepared $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ electrodes synthesized with different ball-milling time shown in Fig. 7. The Nyquist plots of all four samples consist of a depressed semicircle in high-middle frequency region, and followed by a straight line in low-frequency range.

The semicircle in the high-middle frequency region relates to charge-transfer resistance for lithium ion reaction at the interface of electrolyte. It is concluded that the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ sample with synthesized ball-milling time was 15 h exhibits the smallest charge-transfer resistance (200 Ω) than sample with synthesized ball-milling time was 12 h (245 Ω), sample with synthesized ball-milling time was 18 h (251 Ω) and sample with synthesized ball-milling time was 9 h (350 Ω), which indicates that the polarization of sample with synthesized ball-milling time was 15 h is much less than other three samples, it may be beneficial to the rate performance of sample with synthesized ball-milling time was 15 h .

The reasons for this included the following several aspects: The $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ obtained at 15 h with a single phase formation of an α-layered structure without any impurity phase, and particles were spherical shaped and homogeneously distributed, and the sizes of the particles were about 2 μm in diameter and 4μm in length.

$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders were synthesized by many research groups and the related electrochemical data were summarized in Tab. 1 under different synthesizing methods. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples made by co-precipitation method [25] with heated at 950℃ for 24h, the initial discharge capacity of the sample obtained was 155 mAh/g at 0.5C-rate (2.7-4.3V). The initial discharge capacity of the sample which obtained by electrospinning method [26] with a complex route was 139 mAh/g at 0.5C-rate (3.0-4.5V). $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ samples via an original wet-chemical route [27] with heat-treated at 500℃ for 6h and then calcined at 900℃ for 12h, the initial discharge capacity of the sample obtained was 150mAh/g at 0.5C-rate (3.0-4.3V). Microwave-hydrothermal method [28] was used to synthesize $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ with a complex route, the initial discharge capacity of the sample was 160 150mAh/g at 0.1C-rate (2.7-4.3V). The initial discharge capacity of the sample obtained which was synthesized by rheological phase method [29] with heated at 800℃ for 20h was 167mAh/g at 0.1C-rate (3.0-4.3V). In this study, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ particles acquired ball-milling temperature at 750℃ for 15h, and got performance uniformity of the material. Its initial discharge specific capacity reached 166.6 mAh/g at 0.1C-rate (2.7-4.3V). It means $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ which synthesized ball-milling temperature at 750℃ for 15 h has an excellent electrochemical performance.

Compared with $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ powders prepare by other methods, High temperature ball milling method is simple, low-cost and eco-friendly green synthesis approach to synthesize $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. High temperature ball milling method significantly reduced the synthesis temperature and sintering time required in the preparation of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ by high temperature ball milling method probably because ball-milling happened during sintering. The activation energy of the reaction system can be decreased with an increased reaction power: it significantly enhanced the reaction rate and reduced the synthesis time.

4. CONCLUSION

In this paper, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was synthesized with lithium carbonate, nickel (II) oxide, cobalt (II, III) oxide and manganese dioxide as raw materials by high temperature ball milling method.

We investigated the effects of ball-milling time on the performance of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$. In conclusion, when synthesized temperature at 750℃ for 15 h, of which the initial discharge capacity is 166.6 mAh/g at 0.1C-rate, the capacity was 157.5 mAh/g, with a capacity retention rate of 94.5% over 50 cycles. $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ was synthesized by high temperature ball milling method needs shorter time compared to traditional high temperature solid-state method.

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

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