



Microwave synthesis and electrochemical properties of lithium manganese borate as cathode for lithium ion batteries



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HIGHLIGHTS

- A novel microwave solid-state method was adopted to synthesize LiMnBO₃/C.
- The reaction time does not exceed 12 min of the synthesis.
- Synthesized materials showed nano structure.
- LiMnBO₃/C shows excellent electrochemical performance.

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ABSTRACT

Nano structured LiMnBO₃/C cathode materials are synthesized by a fast microwave solid-state reaction method using MnCO₃, Li₂CO₃, H₃BO₃ and glucose as starting materials for the first time. The crystal structure, morphology and electrochemical properties of LiMnBO₃/C composites are characterized by X-ray diffraction (XRD), raman spectroscopy (Raman), scanning electron microscopy (SEM), transmission electron microscopy (TEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge–discharge tests. The result shows that not only monoclinic LiMnBO₃/C but also hexagonal LiMnBO₃/C cathode materials can be successfully synthesized by microwave solid-state method with power of 240 W in different time. Compared with *h*-LiMnBO₃/C and mixed phase LiMnBO₃/C, *m*-LiMnBO₃/C displays lower charge-transfer resistance and the Warburg impedance, so it reveals a higher first discharge capacity of 156.3 mAh g⁻¹ at 0.05 C within 1.8V–4.6 V, The value increases up to 173.2 mAh g⁻¹ caused by the activation process. Even after 50 cycles, the discharge capacity of *m*-LiMnBO₃/C still remains at 148.2 mAh g⁻¹.

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1. Introduction

At present, lithium-ion batteries are widely used for portable electronic devices, electrical vehicle due to their high voltage, high specific capacity, low cost, long cycle life and environmental friendliness [1–3]. Now, cathodes use layered oxides, such as LiCoO₂ [4–6], LiMn₂O₄ [7–9], LiNi_{0.33}Mn_{0.33}Co_{0.33}O₂ [10–12] were mostly used in commercial. However, their high cost, high toxicity and unstable structure prohibit their large-scale application. Therefore, many cathode materials contains polyanion structure such as PO₄³⁻, SO₄²⁻, SiO₄⁴⁻ and BO₃³⁻ have drawn much attention according to their thermal stability and highly safety.

Among polyanion materials, LiFePO₄ has been intensively

studied since 1997 [13], due to its low cost, superior thermal stability and relatively high theoretical capacity (170 mAh g⁻¹) [3,13,14]. But it suffered from poor electronic conductivity (10⁻⁷–10⁻⁹ S cm⁻¹) and stringent synthesis methodology, which against its commercialization [15]. Instead of heavier and larger PO₄³⁻ polyanion materials, BO₃³⁻ polyanion compounds show high theoretical capacity (220 mAh g⁻¹), high stable structure, small electronegativity, and environmental-friendliness [16,17].

LiMnBO₃ has two polymorphs including monoclinic (*m*-LiMnBO₃) and hexagonal (*h*-LiMnBO₃) phases. As early as 1978, Bondanva et al. [18] had obtained monoclinic LiMnBO₃. But Legaigneur et al. [19] first reported that LiMBO₃ (M = Mn, Fe, Co) were able to use as lithium-ion battery cathode materials. However, only 0.02, 0.04 and 0.015 Li per formula unit can be deinserted reversibly from LiMBO₃ (M = Mn, Fe, Co). Many measures have been taken to improve the electrochemical properties of borate materials, such as

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carbon coating [20], reducing crystal size [21] and ion doping [22,23]. Carbon coating is one of the most effective means to improve the electrochemical performance of the LiMnBO_3 materials. Lee et al. [24] synthesised monoclinic/hexagonal mixed-phase LiMnBO_3/C , the highest capacity of 173 mAh g^{-1} after 50 cycles is observed from the $\text{LiMnBO}_3/\text{ketjen}$ black composite. For instance, Aravindan et al. [16] synthesized a carbon coated LiMnBO_3 with an initial discharge of 111 mAh g^{-1} between 1.5 and 4.8 V under ambient temperature at 0.05 C. In 2011, LiMnBO_3/C was successfully synthesized by a solid-state reaction method by Kim [25]. It delivered a second discharge capacity of 100 mAh g^{-1} at 0.05 C in the voltage range of 2.0–4.5 V. Most recently, the research efforts on obtaining LiMnBO_3 had an excellent electrochemical performances have emerged one after another. Semih Afyon [25] et al. synthesized nano-sized *h*- LiMnBO_3 with the first discharge capacity of 145 mAh g^{-1} at C/20 and retaining a discharge capacity of 111 mAh g^{-1} after 10 cycle. Rui Ma et al. [17] prepared carbon coated *h*- LiMnBO_3 , which had the initial charge capacity of 148.4 mAh g^{-1} . However, a few reports were involved in the electrochemical performances of *m*- LiMnBO_3 [25–28]. To our knowledge, *m*- LiMnBO_3 with the best electrochemical performance reported by Lee et al. [29] just reached the first discharge capacity about 150 mAh g^{-1} .

Comparing to other cathode materials, there are still have spaces to promote the performance of LiMnBO_3 . So much works is still needed to explore the optimized synthesis and operation conditions. At present, the synthesizing methods of LiMnBO_3 compounds have mainly used sol-gel method [21] or solid-state method [17,21,26–30], which require high-temperature, long time or inert gas atmosphere. In this study, the *m*- LiMnBO_3/C , which had a relatively good electrochemical performance with a higher first discharge capacity of 156.3 mAh g^{-1} at 0.05 C within 1.8V–4.6 V, was synthesized by fast microwave solid-state method only spending the reaction time of 7–11 min at the power of 240 W. The particles also had high cycle stability after 50 cycles.

2. Experimental

2.1. Synthesis

The LiMnBO_3 powder was prepared by microwave solid state method. Stoichiometric amounts of Li_2CO_3 , MnCO_3 , H_3BO_3 and 10wt% carbon (glucose as the carbon source) were dissolved in deionized water, and then ball milled for 5 h in a planetary mill. The rotating speed was 500 rpm and the ball-to-power weight ratio was 4:1. After evaporating deionized water, the mixture was pressed into pellets. The pellet was added to 10 ml crucible and calcined at microwave oven (China Guangdong, P70D20P-TE (WO)) at the microwave power 240 W for 7, 9 and 11 min.

2.2. Characterization

The phase identification of LiMnBO_3 compounds was carried out using powder X-ray diffraction (XRD, Bruker D2) which had Cu $K\alpha$ radiation. The diffraction data were collected at step mode over the angular range of $10\text{--}70^\circ$ with a step size 0.02° at 30 kV, 10 mA.

Scanning electron microscopy (SEM, Germany Zeissm Supra 55VP) images were collected at 20 kV.

Transmission electron scanning electron microscopy (TEM, Philips CM10) image of the samples were collected under an accelerating voltage of 200 kV.

Raman spectroscopy was performed on a Raman spectrometer (Bruker, JY-HR800) with Ar laser of 50 mW at 532 nm.

For electrochemical measurements, the cathode was fabricated by mixing 75wt% active material, 20wt% acetylene black and 5wt%

polytetrafluoroethylene (PTFE) in deionized water. The obtained slurry was coated on Al foil, and dried at 80°C for 12 h under vacuum. The loading density of active material was approximately $2\text{--}3 \text{ mg/cm}^2$.

All cells were composed with a cathode, a separator (polypropylene porous film), electrolyte and a lithium foil anode. The electrolyte is 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 by volume). The charge and discharge measurement were tested on a battery test system (LAND Wuhan, China CT-2001A) between 1.8 and 4.6 V under constant voltage mode at the rate of C/20 at room temperature.

The cyclic voltammetric (CV) tests and the electrochemical impedance spectroscopy (EIS) tests were all carried out with electrochemical workstation (China Tianjin, LK2005A) before charge–discharge test. The CV curves were recorded in the potential range of 1.8–4.6 V at a scan rate of 0.1 mV/s at room temperature. The EIS tests were recorded with the frequency from 1 Hz to 100 kHz.

3. Results and discussion

LiMnBO_3 has two crystal structures, monoclinic and hexagonal. Fig. 1 shows XRD patterns of the obtained LiMnBO_3/C powders mixture treated in a microwave oven at 240 W for different time. It was possible to obtain both monoclinic and hexagonal structures by firing at various time. When it heated for 7 min, the LiMnBO_3 appeared as pure monoclinic phase in Fig. 1a. All the diffraction peaks matched to *m*- LiMnBO_3 (JCPDS 83-2342) without any detectable impurities. If the time was extended to 9 min, the monoclinic phase was still the superior phase, but a small amount of hexagonal phase at 31° , 36.1° and 38.1° appeared in Fig. 1b. For 11 min, Fig. 1c shows only peaks of hexagonal phase (JCPDS 53-0371) in a well crystallized state. We adjust the power and time to control the temperature of the microwave. The research results of our group are consistent with previous reports [18,19,27], that hexagonal LiMnBO_3 is formed at high temperature but monoclinic LiMnBO_3 is obtained at low temperature. In addition, glucose was used as the carbon source, it could not be detected carbon phase in these LiMnBO_3/C composites, indicating that carbon generated from glucose is amorphous and its presence does not influence the crystal structure of LiMnBO_3 [31].

The morphologies and size of the LiMnBO_3/C materials characterized by SEM and TEM were shown in Fig. 2. It can illustrate from

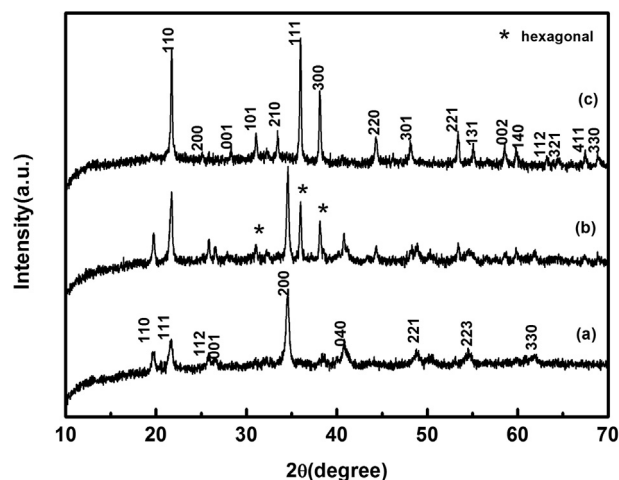


Fig. 1. XRD patterns of LiMnBO_3 by microwave in different time at the microwave power of 240 W: (a) 7 min, (b) 9 min and (c) 11 min.

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