Journal of Power Sources 236 (2013) 54–60

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

In-situ controllable synthesis and performance investigation of carbon-coated monoclinic and hexagonal $LiMnBO_3$ composites as cathode materials in lithium-ion batteries

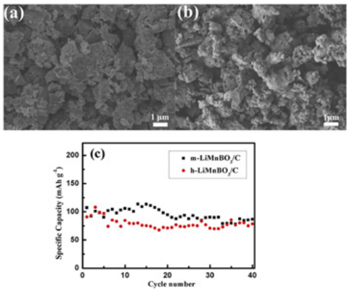
Shouli Li, Liqiang Xu*, Guangda Li, Meng Wang, Yanjun Zhai

Key Laboratory of the Colloid and Interface Chemistry (Shandong University), Ministry of Education, and School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, PR China

HIGHLIGHTS

- ► The m-$LiMnBO_3$/C and h-$LiMnBO_3$/C composites have been selectively and conveniently prepared.
- ► The long cycle stability of h-$LiMnBO_3$/C is firstly reported in this study.
- ► It is the first time to report the rate performance of m-$LiMnBO_3$/C composite.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 November 2012
Received in revised form
10 February 2013
Accepted 12 February 2013
Available online 20 February 2013

Keywords:
Composite materials
Phase control
Borates
Lithium-ion battery

ABSTRACT

The phase controllable synthesis of carbon-coated monoclinic $LiMnBO_3$ (m-$LiMnBO_3$/C) and hexagonal $LiMnBO_3$ (h-$LiMnBO_3$/C) composites has been achieved via an in-situ carbothermal solid state synthesis approach only through the modulation of the reaction temperature. The h-$LiMnBO_3$/C particles keep high cycle stability and retain 86.5% of the initial discharge capacity (90.7 mAh g^{-1}) after 40 cycles at 0.05 C (11 mA g^{-1}) within 1.25–4.80 V, while the m-$LiMnBO_3$/C composites display a first discharge capacity of 107 mAh g^{-1} and a capacity retention rate of 80.8% after 40 cycles. The rate performance of m-$LiMnBO_3$/C has been tested for the first time, which has a capacity of 74.4 mAh g^{-1} at the discharge rate of 0.1 C (22 mA g^{-1}). The enhanced electrochemical performance might be largely attributed to the uniformly coated carbon layers and the reduced particle size of the as-obtained products. The electrochemical impedance spectroscopy (EIS) analysis reveals that the smaller charge transfer resistance (R_{ct}) and higher electronic conductivity of the $LiMnBO_3$/C composites were obtained at 55 °C than those at 25 °C. The as-obtained $LiMnBO_3$/C composites with controllable phases and high performances enable their promising applications as cathode materials for lithium-ion rechargeable batteries.

1. Introduction

Borates ($LiMBO_3$, M = Fe, Mn) are kinds of attractive cathode materials for lithium-ion rechargeable battery owing to their relatively high theoretical capacity (~220 mAh g^{-1}) and little volume changes [1]. They also exhibit relatively high stable structure and adjustable voltage platform characteristics [2]. Since the first report that Li could be reinserted reversibly from the $LiMBO_3$ (M = Co, Fe, Mn) materials in 2001 [3], increasing efforts have been made to improve the electrochemical performances of these materials during the past decade through many new approaches such as carbon addition, nanocrystallization, and ion doping etc. [4–6].

---

* Corresponding author. Tel.: +86 531 88364543; fax: +86 531 88366280.
E-mail address: xulq@sdu.edu.cn (L. Xu).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.02.027

Among these methods, carbon coating is one of the most effective approaches for reducing the structure instability and capacity degradation of individual $LiMBO_3$ materials when encounter with moist air and electrolyte, and for elevating the capacity and cycle stability of the target borate materials. For instance, $LiFeBO_3$/C obtained through a solid state reaction using Li_2CO_3, $FeC_2O_4 \cdot 2H_2O$, B_2O_3, ketchen black and vapour grown carbon fibre as raw materials in Ar atmosphere at 873 K had a discharge capacity of 190 mAh g^{-1} at 0.05 C in the voltage range of 1.5–4.5 V under charging mode at constant voltage of 4.5 V until the current decayed down to 1 mA g^{-1} [7]; Under constant current charge–discharge mode, the initial discharge capacity of $LiFeBO_3$ was improved from 125.8 to 158.3 mAh g^{-1} at 5 mA g^{-1} within a voltage window of 1.0–4.8 V after carbon coating [8].

$LiMnBO_3$ (which has two polymorphs: hexagonal and monoclinic phases) has higher theoretical energy density and average voltage (4.1 V/3.7 V) than those of $LiFeBO_3$ (monoclinic phase) although their theoretical capacities have little difference [9]. The m-$LiMnBO_3$ material was initially synthesized below 400 °C through the hydrothermal process in 1978 [10], but its electrochemical property was not reported until 2011, with a second cycle discharge capacity of about 100 mAh g^{-1} at 0.05 C within 2.0–4.5 V under constant current and constant voltage mode [11]. The bare h-$LiMnBO_3$ material was announced to have a discharge capacity of 75.5 mAh g^{-1} at the current density of 5 mA g^{-1} within a window of 1.0–4.8 V in 2010 [2]. Recently, nanoscaled h-$LiMnBO_3$ particles were firstly obtained via a sol–gel method, which presented a first discharge capacity of 136 mAh g^{-1} in the voltage range of 1.7–4.7 V at 11 mA g^{-1} [5]. Up to date, the $LiMBO_3$ materials were mainly fabricated through solid state process at 500–850 °C for 12–15 h under inert atmosphere [2,12], while the two-step calcination processes were usually required together with the intermediate ball-milling process to minimize the particle size after the first calcination process. The carbon-coated h-$LiMnBO_3$was usually fabricated via the calcination of the mixture of h-$LiMnBO_3$ and carbon sources under inert atmosphere [11]. To further facilitate the fabrication process and improve the carbon coating efficiency, new developments and strategies are required for these materials. In this study, $LiMnBO_3$/C composites with tunable phases have been obtained through in-situ carbothermal solid state synthesis approach under relatively low temperature. For example, the h-$LiMnBO_3$/C particles were obtained at 750 °C. These particles keep high cycle stability and retain 86.5% of the initial discharge capacity (90.7 mAh g^{-1}) after 40 cycles at 11 mA g^{-1} within 1.25–4.80 V under constant current charge-discharge mode. The actual discharge capacity of h-$LiMnBO_3$ is obviously enhanced via in-situ carbon coating process compared with that of the previous report [2]. While the m-$LiMnBO_3$/C particles could be obtained at 500–600 °C. The m-$LiMnBO_3$/C particles prepared at 600 °C have an initial discharge capacity of up to 107 mAh g^{-1}. It is notable that even if the current density is increased to 22 mA g^{-1}, the specific discharge capacity of 74.4 mAh g^{-1} still can be obtained. The above results indicate that the $LiMnBO_3$/C materials with controllable phases obtained via the convenient in-situ carbothermal solid state synthesis method are promising cathode materials for lithium-ion rechargeable batteries.

2. Experimental

2.1. Sample preparation

All the raw materials used here were of analytic grade without further purification. h-$LiMnBO_3$/C and m-$LiMnBO_3$/C powders were controllable prepared via adjusting the heating temperature through in-situ carbothermal solid state synthesis with the stage-temperature-programmed calcination process [11,13]. In a typical process,10 mmol $LiOH \cdot H_2O$, 10 mmol $MnCO_3$, 10 mmol H_3BO_3 and 2.5 mmol ascorbic acid were dispersed into ethanol and ball-milled for 5 h, then the solvents were evaporated in the vacuum oven at 60 °C. For the preparation of h-$LiMnBO_3$/C, the precursor was calcined at 250 °C for 3 h at first, and then at 750 °C for 10 h with a increasing heating rate of 5 °C per minute under Ar atmosphere in a tube furnace. For the synthesis of m-$LiMnBO_3$/C, the precursor was calcined at 250 °C for 3 h and then at 500–600 °C for 10 h.

2.2. Characterization

The X-ray diffraction (XRD) patterns were measured on a Bruker D8 advanced X-ray diffractometer equipped with graphite-monochromatized CuKα radiation (λ = 1.5418 Å). The Raman spectrum was recorded at ambient temperature on a LABRAM-HR confocal laser MicroRaman spectrometer with an argon-ion laser at an excitation wavelength of 514.5 nm. The transmission electron microscopy (TEM, JEM-2011), field emission scanning electron microscope (FESEM; JEOL JSM-6700F) and high-resolution TEM (HRTEM, JEM-2100, 200 kV) were used to characterize the morphology and size of the samples.

2.3. Electrochemical measurements

The electrochemical discharge-charge performances of the samples were tested on a Land battery test system (CT2001A) at 25 °C. The working electrodes were consisted of 70 wt% active materials (h-$LiMnBO_3$/C or m-$LiMnBO_3$/C), 20 wt% carbon black, and 10 wt% poly(vinylidene fluoride) (PVDF). n-Methylpyrrolidone (NMP) was used as the solvent. The mixed slurry with thickness of 200 μm was coated onto a piece of Al foil and dried in vacuum oven at 80 °C for 12 h, then cut into discs with diameter of 12 mm. The weight of electrode pieces was in the range of 2–3 mg except that of the pristine Al foil. And the mass calculation of the active $LiMnBO_3$/C materials was carried out based on 70% of the mass of electrode piece. Nickel foams were used as the current collector, and Celgard 2300 microporous polypropylene membrane was used as the separator. The electrolyte was composed of 1 mol $L^{-1}LiPF_6$ dissolved ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, volume ratio was 1:1:1). Lithium foils with the diameter of 15 mm and the thickness of 0.4 mm were used as the counter electrodes. The button batteries were assembled in an argon-filled glove box and cycled at different charge-discharge current densities (5, 11, 22 mA g^{-1}) within voltage limit of 1.25–4.80 V. The electrochemical impedance spectroscopy (EIS) was measured with a Princeton Applied Research by applying an alternating current voltage of 10 mV in the frequency from 10 mHz to 100 kHz at open-circuit voltage (~3 V) before charge-discharge test.

3. Results and discussion

3.1. Structure and morphology characterizations

The typical XRD patterns of the as-obtained $LiMnBO_3$/C samples are shown in Fig. 1a–b. All the diffraction peaks can be assigned to highly crystalline m-$LiMnBO_3$/C and h-$LiMnBO_3$/C without any detectable impurities. The typical XRD pattern of pure m-$LiMnBO_3$/C shown in Fig. 1a is consistent with that mentioned in the reference (JCPDS card no. 83-2342, space group: C2/c) [10,11]. Fig. 1b shows the XRD pattern of h-$LiMnBO_3$/C (JCPDS no. 53-0371, space group: P-6). No obvious peaks of graphite can be observed from the above pattern owing to their low loading amount or low crystallinity [14]. Raman spectra analyses were carried out to further