

Synthesis and Electrochemical Properties of LiMnBO₃/C composite

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Abstract: LiMnBO₃/C composite material was prepared by a rheological phase reaction method and successive annealing procedure. In the synthesis procedure, citric acid was selected as carbon source. The electrochemical tests showed that the LiMnBO₃/C could greatly improve the discharge capacity, rate capability and cycling stability due to the improved electric conductivity. The LiMnBO₃/C shows good electrochemical performance (the initial discharge capacity of 127.3 mAh g⁻¹ at 10 mA/g). These results indicate that the samples could be a promising cathode material for lithium ion batteries.

Introduction

Lithium metal borates LiMBO₃ (M=Mn, Fe, Co, Zn) have received much attention because the lightest polyanion group (BO₃⁻) is expected to provide higher theoretical energy density (222 mA h g⁻¹) than other polyanion cathode materials^[1-7]. Legagneur et al.^[3] had reported the structural data and lithium insertion/deinsertion properties of LiMBO₃ (M=Mn, Fe, Co) as new cathode materials. From their experimental results, only a very small amount of lithium was reinserted reversibly from the three compounds. Zhao et al. [8] reported hexagonal LiMnBO₃ (h-LiMnBO₃) synthesized by a one-step solid state reaction. These results imply that the synthesis condition and nanosizing of the materials can be critical for this class of electrode material to achieve high-power capacity. Afyon et al. [9] synthesized nano h-LiMnBO₃ and a composite of nano h-LiMnBO₃ with reduced graphite oxide (RGO) by a sol-gel method for the first time. The nano h-LiMnBO₃ electrode delivers a first discharge capacity of 136 mAhg⁻¹ at C/20 rate.

In this work, we have prepared LiMnBO₃ and LiMnBO₃/C composites using the rheological phase reaction method and successive calcination procedure. When the prepared materials were evaluated as cathode for lithium ion batteries, they shows good electrochemical performance, in terms of rate capability, and cycling stability.

Experimental

Synthesis and characterization of the samples

All chemicals were of analytical grade and were used without further purification. At first, LiOH·2H₂O, Mn(CH₃COO)₂·4H₂O, and H₃BO₃ in the molar ratio of 1:1:1 were mechanically mixed with an agate mortar and pestle by adding water to obtain a rheological mixture. An appropriate amount of citric acid (ca. 25 mol % of total metal ions present in the mixture) was used as a carbon source for the preparation of the carbon coated samples. The rheological phase mixtures were heated at 100 °C for 12 h to obtain the precursors. The precursors were firstly calcined at

350 °C for 3 h and then heated at 800 °C for 15 h under argon atmosphere. For convenience, samples were labeled as LiMnBO_3 and LiMnBO_3/C .

Powder X-ray diffraction patterns of the samples were obtained with a Rigaku XRD diffractometer. The morphologies of the samples were observed by using a scanning electron microscope (SEM; LEO 1530VP, Germany).

The electrochemical characterization was performed using CR2032 coin-type test cells. The cell consisted of a cathode with the composition of 70 wt.% active materials, 20 wt.% carbon black, and 10 wt.% PVDF, a lithium metal anode separated by a Celguard 2400 microporous film. The electrolyte was 1 molL^{-1} $\text{LiPF}_6/(\text{EC})$ and (DEC) (1:1). Charge-discharge tests were carried out at different current densities in the range of 1.0 V to 4.6 V.

Results and discussion

The crystallographic structures of the LiMnBO_3 and LiMnBO_3/C samples are first confirmed by XRD analysis as shown in Figure 1. The diffraction peaks of sample can be indexed as hexagonal LiMnBO_3 with cell parameters $a = 5.166(2) \text{ \AA}$, and the space group was derived to be $C2/c$. The observed XRD patterns were well consistent with the previously reported patterns^[3].

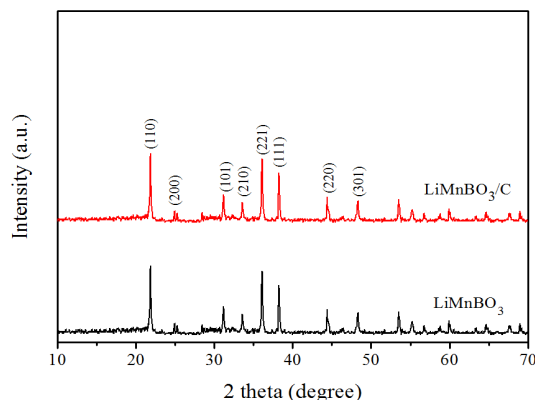
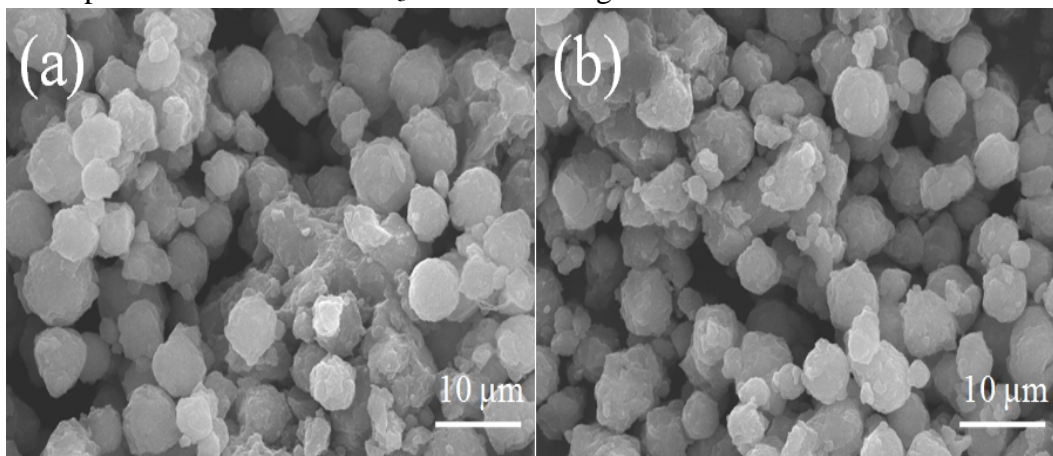


Fig. 1. XRD patterns of LiMnBO_3 and LiMnBO_3/C .

The surface morphological features of LiMnBO_3 and LiFeBO_3/C were investigated by SEM. As shown in Fig.2, they are all composed of non-uniform particles with different sizes. From Fig. 2b and 2d, it can be observed that the particles of the bare LiMnBO_3 sample were agglomerated with the particles sized with ca. 0.5–10 μm , which were much larger than those of LiMnBO_3/C . Fig 2d shows that the particle size of LiMnBO_3/C is in the range of 100–500 nm.



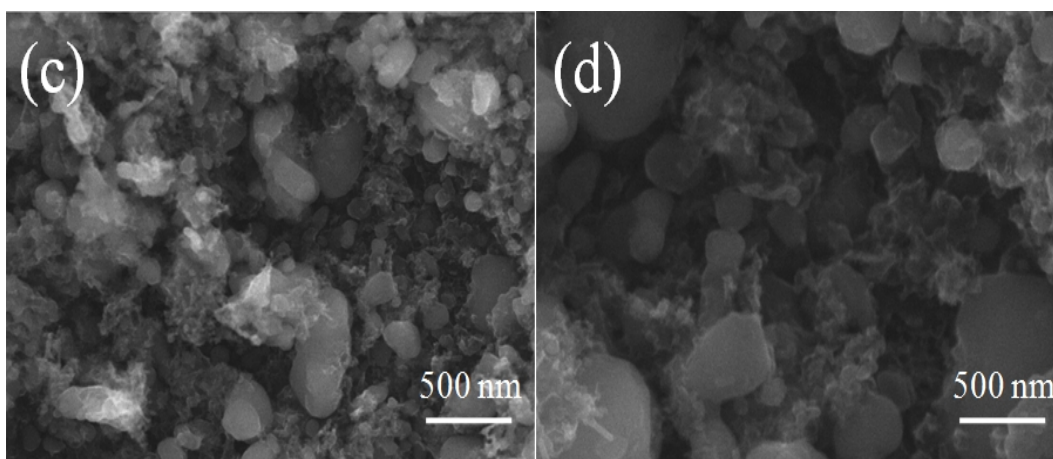


Fig. 2. SEM images of the samples: (a, b) LiMnBO₃ and (c, d) LiMnBO₃/C.

The electrochemical performances of LiMnBO₃ and LiMnBO₃/C were measured via coin cell testing. Fig.3 (a, b) showed the typical discharge/charge cycles of the as-prepared LiMnBO₃ and LiMnBO₃/C electrodes cycled between 1.0 and 4.6 V with a current density of 10 mA g⁻¹ at room temperature, respectively. In the discharge curves, two voltage plateaus near at 3.0 and 2.7 V are clearly observed in all samples. LiMnBO₃ electrode delivers an initial discharge capacity of 83.3 mA h g⁻¹ (Fig.3c). The discharge capacity reduces to 72.6 mA h g⁻¹ after 50 cycles, the capacity retention was 87.1%. For LiMnBO₃/C, the initial discharge capacity was 127.3 mA h g⁻¹ (Fig.3c). After 50 cycles, the discharge capacity dropped to 105.9 mA h g⁻¹. It is obvious that LiMnBO₃/C show improved cycling performance with higher specific capacities at the same cycle with the same current density as compared with the bare LiMnBO₃. Obviously, carbon coating provides the improved conductivity and connectivity between the active particles present in the electrode, which give rise to improve the capacity of the material.

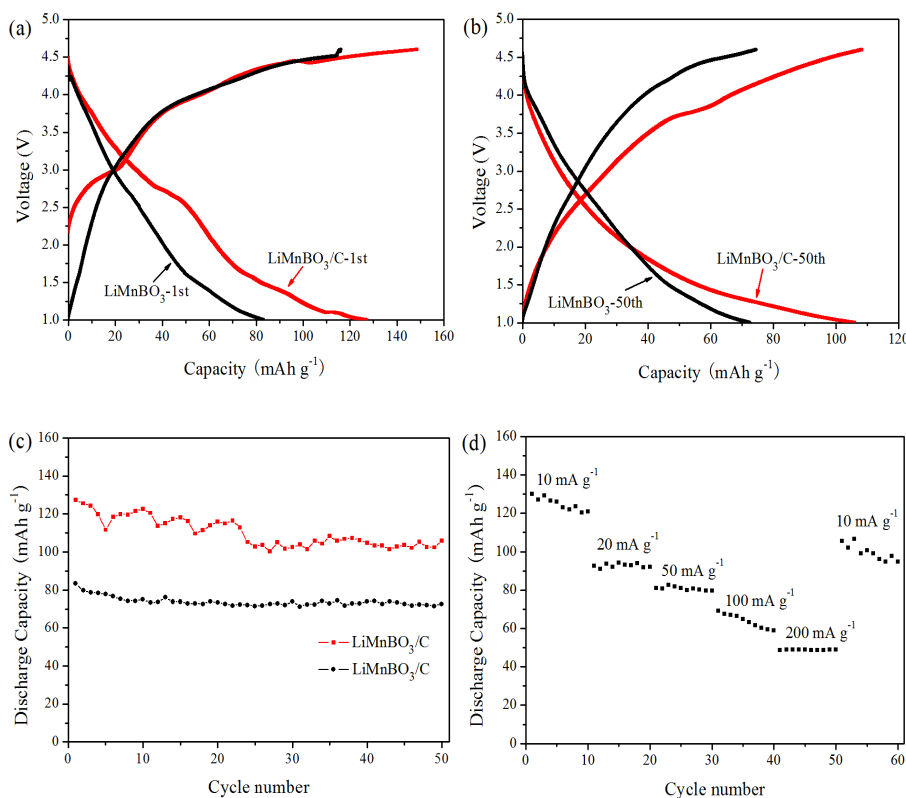


Fig. 3. Typical discharge/charge cycles of (a) LiMnBO₃ and (b) LiMnBO₃/C, Cycling performance (c) of LiMnBO₃ and LiMnBO₃/C and rate performance (d) of LiMnBO₃/C.

Fig.3d shows the rate capability of the LiMnBO₃/C electrode at various current densities. Apparently, the LiMnBO₃/C electrode displays good capacity retention at different current densities. When the current rates were 10, 20, 50, 100, and 200 mA g⁻¹, the specific capacities were 129.2, 94.3, 80.6, 69.1, and 48.5 mA h g⁻¹, respectively. Upon altering the current density back to 10 mA g⁻¹ after the rate performance testing, an average discharge capacity as high as 105.8 mAh g⁻¹ could be recovered.

Conclusion

LiMnBO₃ and LiMnBO₃/C were successfully prepared by a rheological phase reaction method. LiMnBO₃/C displays the best electrochemical performance. It shows a large discharge capacity of 127.3 mA h g⁻¹ at 10 mA g⁻¹, the discharge capacity dropped to 105.9 mA h g⁻¹ after 50 cycles, and good cycling stability at various current densities. The research results provides one possible direction for future cathode of lithium ion batteries. These results indicate that LiMnBO₃/C could be a promising cathode material for lithium ion batteries.

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