

# Li-B Alloy as an Anode Material for Stable and Long Life Lithium Metal Batteries

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Received: 30 August 2018; Accepted: 14 September 2018; Published: 21 September 2018



**Abstract:** Rechargeable Li metal batteries have attracted lots of attention because they can achieve high energy densities. However, the commercialization of rechargeable Li metal batteries is delayed because Li dendrites may be generated during the batteries' electrochemical cycles, which may cause severe safety issues. In this research, a Li-B alloy is investigated as an anode for rechargeable batteries instead of Li metal. Results show that the Li-B alloy has better effects in suppressing the formation of dendritic lithium, reducing the interface impedance and improving the cycle performance. These effects may result from the unique structure of Li-B alloy, in which free lithium is embedded in the  $\text{Li}_7\text{B}_6$  framework. These results suggest that Li-B alloy may be a promising anode material applicable in rechargeable lithium batteries.

**Keywords:** Lithium ion batteries; anode; Li-B alloy; Li metal; electrochemical cycle

## 1. Introduction

Energy storage systems with high energy densities are urgently needed to satisfy the continuously growing demands of consumer electronics, electric vehicles and grid storage systems [1–5]. In this area, rechargeable Li metal batteries have attracted more and more attention because Li metal has an extremely high theoretical capacity ( $3860 \text{ mAh g}^{-1}$ ) and the lowest negative potential ( $-3.04 \text{ V}$  versus the standard hydrogen electrode) [6–10]. However, rechargeable Li metal batteries have not been commercialized because of the potential formation of Li dendrites [11–13] which may pierce through the separator and create a dangerous internal circuit [14]. In addition, during the deposition/dissolution of Li, the original solid electrolyte interface (SEI) is destroyed, and some amount of fresh Li metal will be exposed to the electrolyte and new SEI layers will be continuously produced during cycling. This repeated breakage and repair of the SEI layers will continuously consume both Li metal and electrolyte, leading to lower coulombic efficiency and poorer cycling performance [15]. Many efforts have been made to improve the performance of Li metal by modifying the Li metal surface [16,17]. Wang et al. deposited a 30 nm amorphous  $\text{Li}_3\text{PO}_4$  thin film on a Li metal surface via magnetron sputtering to suppress the lithium dendrite growth and improve the battery life span [18]. Li et al. used a chemical method to build an artificial SEI layer on Li metal and obtained a much better cycling performance [19]. Herein, instead of Li metal, Li-B alloy is investigated as an anode for rechargeable batteries.

Lithium-boron (Li-B) alloy is commonly used as an anode in thermal batteries [20]. It is a two-phase material made by heating together lithium and boron. Its structure can be described as free lithium embedded in the  $\text{Li}_7\text{B}_6$  framework [21]. Li-B alloy has good electric conductivity

and an acceptable Li ion diffusion rate. When Li-B alloy is used as anode, its free metal lithium participates preferentially in electrochemical reactions [22]. Compared with Li metal, Li-B alloy has a different chemical composition and surface microstructure, which may impact the deposition of Li metal, and hence present different Li metal deposition/dissolution properties [23]. Thus, in this paper, we analyzed the structures and morphologies of Li-B alloy and studied its electrochemical performance as an anode in rechargeable batteries.

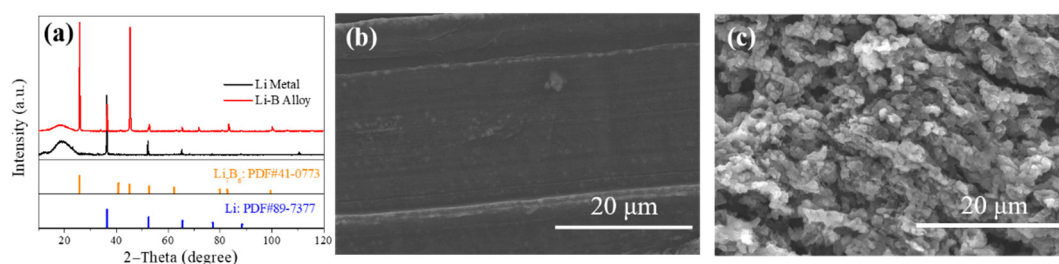
## 2. Experimental

Li-B alloy was obtained from China Energy Lithium Co. Ltd. (Tianjin, China), and it was punched into a small 14 mm diameter disk. The Li-B alloy and Li metal were characterized by X-ray diffraction (XRD) on a D8 X-ray diffractometer (Bruker, Karlsruhe, Germany) using K- $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The surface morphologies of the electrodes were measured by scanning electron microscopy (SEM) using a SU8010 scanning electron microscope (Hitachi, Tokyo, Japan). After electrochemical treatments, the electrodes were washed with dimethyl carbonate (DMC) and dried, and then transferred into the SEM chamber as quickly as possible. The total transfer time lasted only a few seconds.

For electrochemical measurements, the cathodes were composed of  $\text{LiFePO}_4$ , super P and polyvinylidene fluoride (PVDF) at a weight ratio of 8:1:1. Aluminum foil was used as current collector, and the diameter of each electrode was 12 mm. CR2032 coin cells were assembled in a glovebox (Vigor, Suzhou, China) filled with a high purity argon atmosphere ( $\text{O}_2$  and  $\text{H}_2\text{O} < 0.05 \text{ ppm}$ ). The Li-B alloy or Li metal were used as both counter and reference electrode. The electrolyte was 1 M  $\text{LiPF}_6$  dissolved in ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1:1. All the cells were cycled using an automatic battery tester (Land, Wuhan, China) at room temperature at a current density of 0.5 C ( $85 \text{ mA g}^{-1}$  of  $\text{LiFePO}_4$ ). The cycling performances were tested by the constant current (CC) mode in the voltage range of 4.3–2 V. Electrochemical impedance spectroscopy (EIS) measurements were tested on a reference 3000 electrochemical workstation (Gamry, Warminster, PA, USA) in the frequency range from 100 kHz to 5 mHz with a perturbation amplitude of 5 mV.

## 3. Results and Discussion

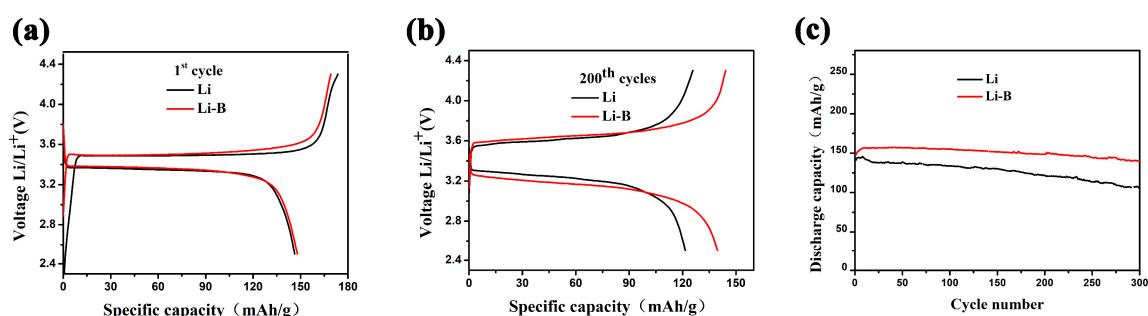
Figure 1a shows the XRD patterns of Li metal and Li-B alloy. The bumps around  $20^\circ$  are related to the Kapton<sup>®</sup> films with which the samples were covered during the XRD experiments. Characteristic peaks of the Li and  $\text{Li}_7\text{B}_6$  are marked beneath for comparison. It could be seen that the diffraction pattern of Li metal reported in this manuscript corresponds well to the PDF card of Li. As to the Li-B alloy, it is reported to be composed of two phases, rhombohedral  $\text{Li}_7\text{B}_6$  compound (JCPDS 41-0773) and cubic lithium (JCPDS 15-0401). The peaks of the Li-B alloy in this research correspond well with these two phases. The SEM images of Li metal and Li-B alloy are shown in Figure 1b,c, respectively. It could be seen that the surface of Li metal is relatively smooth. As to the Li-B alloy, the surface is not very smooth, which may be due to the rolling process used in the preparation of the alloy foil.



**Figure 1.** XRD pattern of Li metal and Li-B alloy (a); SEM images of Li metal (b) and Li-B alloy (c).

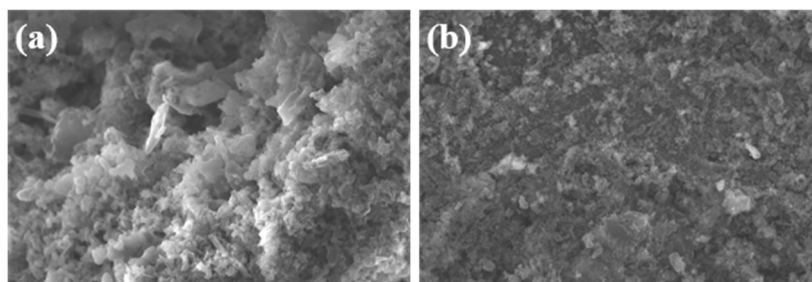
In batteries, when Li metal or Li alloy is used as the anode, Li metal will deposit onto and dissolve from the anode during the successive electrochemical cycles. Different materials with different

structures and different surface micromorphologies may lead to different polarization voltages and cycling performances. As to Li-B alloy,  $\text{Li}_7\text{B}_6$  makes up the framework and free Li is embedded in it, which is a unique structure that may present a different Li dissolution/deposition performance. In this study, the Li-B alloy used contains 47% free metal lithium ( $\text{Li}_7\text{B}_6 \cdot 15\text{Li}$ ) and possesses a theoretical capacity of  $3495 \text{ mAh g}^{-1}$  [22]. The effects of Li-B alloy were verified by a comparative study between  $\text{LiB/LiFePO}_4$  and  $\text{Li/LiFePO}_4$  cells cycled at a rate of 0.5 C (1 C means accomplishing discharge and charge in an hour). The 1st charge-discharge profiles of both batteries are exhibited in Figure 2a. It could be seen that the charge and discharge plateaus of the  $\text{LiB/LiFePO}_4$  battery are similar to those of the  $\text{Li/LiFePO}_4$  battery, which means the polarization voltage of Li-B alloy is analogous to that of the Li metal one. However, after 200 cycles, the charge and discharge curves of the two batteries (Figure 2b) show some differences. The charge and discharge capacities of the  $\text{LiB/LiFePO}_4$  battery are much larger than those of  $\text{Li/LiFePO}_4$ . The reason may be that in the  $\text{Li/LiFePO}_4$  cell, during the deposition/dissolution of Li, the original solid electrolyte interface (SEI) is destroyed and new SEI layers will be continuously produced during cycling, which causes the repeated breakage and repair of the SEI layers, continuously consumes both Li metal and electrolyte, and finally leads to smaller capacities. On the other hand, the discharge plateau of the  $\text{LiB/LiFePO}_4$  battery is slightly lower than that of the  $\text{Li/LiFePO}_4$  battery, which indicates that during the electrochemical cycles, the surface composition of the Li-B alloy may be changed and the polarization voltage thus enlarged, but the detailed mechanism of this phenomenon still needs further research. The discharge capacities during the cycles are presented in Figure 2c. The  $\text{LiB/LiFePO}_4$  battery shows much better cycling performance, and could maintain 95% capacity after 300 cycles. As to the  $\text{Li/LiFePO}_4$  battery, it could only maintain 75% of its pristine capacity after 300 cycles. These results indicate that the Li-B alloy might suppress the formation of lithium dendrites during long cycles.



**Figure 2.** Charge and discharge profiles of  $\text{Li/LiFePO}_4$  and  $\text{LiB/LiFePO}_4$  battery of the 1st cycle (a) and 200th cycle (b); cycling performances of these two batteries (c).

In order to further confirm these effects, cells were disassembled after 300 cycles and the surface morphologies of the two electrodes were observed. The results are shown in Figure 3.

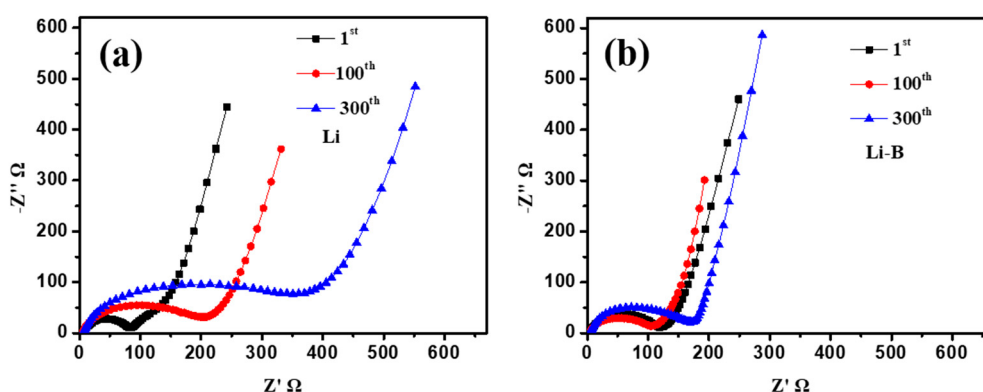


**Figure 3.** SEM images of the Li metal electrode (a) and Li-B alloy electrode (b) after 300 cycles.

The surface of Li metal is totally different from the pristine state. It had become much rougher and dendritic lithium could be obviously observed, but the surface of Li-B alloy remained unchanged.

This result demonstrates that lithium tends to deposit uniformly on the surface of Li-B alloy, which might suppress the dendritic Li deposition, and improve the safety performance. Also, the suppression of dendritic Li deposition and pulverization may avoid the consumption of electrolytes on the exposed surface area of anode, and enhance the electrochemical performances.

We also used electrochemical impedance spectroscopy (EIS) measurements to study the interface stabilities of Li metal and Li-B alloy during dissolution/deposition cycles. As shown in Figure 4, after the 1st cycle, the cell with metallic Li electrode has lower resistivity than the one with Li-B alloy. The reason may be Li metal has higher electrical conductivity than Li-B alloy. After 100 and 300 cycles, the charge transfer resistances of both cells increase, but with different times. After 300 cycles, the resistance of Li/LiFePO<sub>4</sub> battery increases to about four times the value of the 1st cycle, while the resistance of LiB/LiFePO<sub>4</sub> battery only becomes slightly larger than that of the 1st cycle. These results demonstrate that the Li-B alloy has a more stable interface during the electrochemical cycles.



**Figure 4.** Electrochemical impedance spectra of Li metal (a) and Li-B alloy (b) after the 1st, 100th, and 300th cycles.

#### 4. Conclusions

In the research, the electrochemical performance of a Li-B alloy as anode in batteries was studied. Results show that Li-B alloy has better effects in suppressing the formation of dendritic lithium, reducing the interface impedance and improving the cycle performance. These effects may come from the unique structure of Li-B alloy, in which free lithium is embedded in the Li<sub>7</sub>B<sub>6</sub> framework of the alloy. These results indicate that Li-B alloy may be a promising anode material for rechargeable lithium batteries.

**Author Contributions:** R.W. conceived and designed the research. Q.L. and C.T. carried out the electrochemical tests. S.Z. and Q.Z. performed the electrochemical impedance spectroscopy experiments. R.W. wrote the manuscript with the help of X.Z. All authors reviewed the manuscript.

**Funding:** This research was funded by National Key Research and Development Program of China (2016YFC0300200) and National Natural Science Foundation of China (51702294).

**Conflicts of Interest:** The authors declare no competing interests.

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