The structure and electrochemical performance of LiFeBO₃ as a novel Li-battery cathode material

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Abstract

LiFeBO₃ cathode material has been synthesized successfully by solid-state reaction using Li₂CO₃, H₃BO₃ and FeC₂O₄·2H₂O as starting materials. The crystal structure has been determined by the X-ray diffraction. Electrochemical tests show that an initial discharge capacity of about 125.8 mAh/g can be obtained at the discharge current density of 5 mA/g. When the discharge current density is increased to 50 mA/g, the specific capacity of 88.6 mAh/g can still be held. In order to further improve the electrochemical properties, the carbon-coated LiFeBO₃, C-LiFeBO₃, are also prepared. The amount of carbon coated on LiFeBO₃ particles was determined to be around 5% by TG analysis. In comparison with the pure LiFeBO₃, a higher discharge capacity, 158.3 mAh/g at 5 mA/g and 122.9 mAh/g at 50 mA/g, was obtained for C-LiFeBO₃. Based on its low cost and reasonable electrochemical properties obtained in this work, LiFeBO₃ may be an attractive cathode for lithium-ion batteries.

Keywords: Lithium-ion batteries; LiFeBO₃; Electrochemical performance

1. Introduction

The need for high performance rechargeable batteries for portable electronic devices, electrical vehicle, and dispersed-type energy systems has led to the development of lithium-ion battery.

At present, most of lithium batteries used in electronic devices or hybrid electric vehicles employ transition metal oxides such as LiCoO₂, LiMn₂O₄ or mixed metal analogs such as Li(Ni,Mn,Co)O₂ as the active cathode materials [1–4]. But their high cost and toxicity prohibit their use in a large-scale or biomedical application. Thus, many efforts have been made to find a kind of alternative materials with high safety, high performance, less expensive and less toxic, and it is believed that there exist other compounds in the still unexploited reservoir of Li-compounds containing lithium elements and transition metal elements. LiFePO₄ [5,6] has been the focus of candidates as cathode materials with potentially low cost and plentiful elements and also environmentally benign that could have the major impact in electrochemical energy storage. No obvious capacity fading was observed even after several 100 cycles for LiFePO₄. Its stability is afforded by such a scaffolded structure deriving from the strong covalent P–O bond, which translates into electrochemical and chemical safety in a voltage domain where no protective passivation layer is needed [7]. From 1997 [8], the published results show that almost 100% of theoretical capacity at low rates and considerable capacities at very high rates (about 8500 mA/g up to 50 °C) can be obtained and thus, LiFePO₄ has been the alternative material to replace LiCoO₂ in rechargeable batteries.

It is well known that boron atom can be coordinated by oxygen atoms to form a variety of atomic groups, which are considered to be a dominant factor for physical properties. In addition, it has been shown that polyanions enable low transition metal redox energies through the inductive effective effect, thereby allowing some sort tuning of such energies. So like most studied polyanions which utilized tetrahedral group (XO₄)²⁻ or (XO₃)³⁻ with X = Mo, W, S, P or V [9–11], recently many studies tend to give a preliminary evaluation of the inductive effect of the much lighter BO₃ group [12–14]. This makes the...
borate become an attractive new cathode material for lithium-ion batteries.

Legagneur et al. first reported LiMBO₃ (M = Mn, Fe, Co) as a new cathode material. From their experimental results, only a very small amount of lithium (less than 0.04 Li per formula unit) was deinserted reversibly from the three compounds [15]. However, from the thermodynamic study performed in the case of LiFeBO₃, the Fe³⁺/Fe²⁺ reduction couple lies between 3.1 V/Li and 2.9 V/Li, demonstrating an important inductive effect of the BO₃ group. It should be a good cathode material for lithium-ion batteries. This prompts us to investigate the structure and electrochemical properties of LiFeBO₃ in detail.

In this paper, we successfully synthesized the LiFeBO₃ compound by using conventional solid-state reaction. Our measured results show that at the discharge current density of 5 mA/g, an initial specific capacity of 125.8 mAh/g can be obtained from this compound. Even when the discharge current density is increased to 50 mA/g, a specific capacity of 88.6 mAh/g can still be held. In addition, by using carbon in synthesized process a higher discharge capacity, 158.3 mAh/g at 5 mA/g and 122.9 mAh/g at 50 mA/g, was obtained for carbon-coated LiFeBO₃.

2. Experimental

The LiFeBO₃ samples were made by mixing stoichiometric amounts of Li₂CO₃, FeC₂O₄·2H₂O and H₃BO₃; the precursors were dispersed into acetone and then ball milled for 6 h in a planetary mill. The rotating speed was 250 rpm and the ball-to-power weight ratio was 20:1. After evaporation acetone, the mixture was first decomposed at 350 °C in a N₂ atmosphere for 10 h to allow H₂O to evaporate. The reagents were then re-ground and pressed into pellets of 10 mm in diameter and 1–2 mm in thickness. The pellets were heated at a rate of 2 °C/min to 650 °C under a stream of a mixture of 95%Ar+5%H₂ in a sealed tube furnace. The materials were held for 10 h at the upper temperature and slowly cooled down to room temperature before removing from the furnace. The gray powders, LiFeBO₃, were obtained. For the carbon-coated LiFeBO₃, carbon gel (with the total amounts of 5 wt.% for the final product LiFeBO₃) was added to the mixture of the starting materials. After the same mechanochemical treatment, the carbon-coated LiFeBO₃ powders, C-LiFeBO₃, were synthesized with the same heat-treatment conditions.

The initial characterization of the material was carried out using powder X-ray diffraction (XRD), employing a MAX 18A-HF diffractometer with rotating anode, which had an 18 kW X-ray generator and Cu Kα radiation. A graphite monochromator was used for diffracted beams. All the diffraction intensity data for Rietveld refinement analysis were collected by a step scan mode with a scanning step of 0.02° and a sampling time of 2 s. Rietveld refinement was performed using the FullProf program to obtain the crystal structure parameters.

The electronic conductivity measurement was adopted with a RTS-8 linear four-point probe measurement system. The conductivity was measured three times at different position of the LiFeBO₃ pellet with 10 mm in diameter and 1 mm in thickness and the results are 1.52 × 10⁻⁴ S/cm, 1.51 × 10⁻⁴ S/cm and 1.54 × 10⁻⁴ S/cm, respectively. The average electronic conductivity of about 1.52 × 10⁻⁴ S/cm was obtained.

In order to determine the carbon content, the DTA measurement was performed employing a CR-G type high-temperature µ-DTA apparatus. Alumina crucibles were used as vessels and α-Al₂O₃ as a reference substance. Pt–PtRh thermocouples were used for measurement. The precision of measurement was ±3 °C. The heating rate was 10 °C/min from room temperature to 1000 °C.

For electrochemical measurements, the LiFeBO₃ electrodes were prepared by mixing with a conductive carbon, acetylene black, and a binder, PVDF-HFP copolymer. The electrode constituents were mixed into a slurry with acetone to achieve homogeneity. The resulting slurry was coated onto aluminum foil current collector using a doctor blade. After the acetone had evaporated, the resulting electrode composition was 75:15:10 of active material, carbon, and binder, respectively. The electrode was then dried at 50 °C for 24 h and pressed (5 MPa), respectively. The electrodes fabricated were dried again at 90 °C for 12 h in a vacuum and cut into 1 cm × 1 cm in size where about 5 mg of active materials was hold on it. Two-electrode electrochemical cells were assembled in a Mikrouna glove box filled with high-purity argon, where the lithium metal foil were used as an anode, Celgard® 2320 as a separator, and 1 M LiPF₆ in EC:DMC (1:1 vol.%) were used as an electrolyte. The electrochemical capacity measurements were performed in the voltage range between 1 V and 4.8 V, and the electrochemical capacity of samples was evaluated on the active materials.

3. Results and discussion

The XRD pattern of LiFeBO₃ confirms that the sample is a pure phase and well crystallized. The diffraction patterns were successfully indexed with monoclinic lattice using the program Dicovl, and the space group of LiFeBO₃ compounds was derived to be C2/c based on the reflection conditions. The single-phase model Rietveld refinement of the LiFeBO₃ compound was made, and a space group of C2/c was chosen as the refinement model. Fig. 1 shows the result of the Rietveld refinement of X-ray diffraction pattern for this compound. This refinement led to a rather good agreement between the experimental and the calculated XRD pattern and low reliability factors (Rp = 11.6%, Rwp = 11.6% and Rexp = 7.39%) can be obtained. The structural parameters of LiFeBO₃ obtained from the refinement result are listed in Table 1. The structure of LiFeBO₃ is analogous with that of LiMnBO₃. In this monoclinic structure each unit cell contains four chemical formula units of LiFeBO₃ and all atoms occupy the 8f sites. The cell parameters (a = 5.1704 Å, b = 8.9183 Å, c = 10.1797 Å) obtained from the refinement are in good agreement with the earlier work [15]. However, an obvious difference of atoms positions and occupancy for Li and Fe atoms (Li1: 48%, Li2: 52%, Fe1: 72%, Fe2: 28% for Legagneur’s result and Li1: 50%, Li2: 50%, Fe1: 50%, Fe2: 50% for our result) is observed in this work [15]. Fig. 2 shows the framework of LiFeBO₃, in which Fe atoms occupy statistically two close positions with the occupancy of 50% for Fe1 and 50% for Fe2, respectively. The distance between Fe1 and Fe2 is 0.3269 Å. All the Fe atoms
Fig. 1. XRD refinement result of LiFeBO₃ powder.

Table 1
Structure parameters of LiFeBO₃ determined from X-ray diffraction

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupation</th>
</tr>
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<tbody>
<tr>
<td>Li₁</td>
<td>8f</td>
<td>0.71627</td>
<td>0.48964</td>
<td>0.12045</td>
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<tr>
<td>Li₂</td>
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<td>0.70598</td>
<td>0.53382</td>
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<tr>
<td>Fe₁</td>
<td>8f</td>
<td>0.14601</td>
<td>0.33377</td>
<td>0.13963</td>
<td>0.50</td>
</tr>
<tr>
<td>Fe₂</td>
<td>8f</td>
<td>0.17452</td>
<td>0.33874</td>
<td>0.11162</td>
<td>0.50</td>
</tr>
<tr>
<td>B</td>
<td>8f</td>
<td>0.17283</td>
<td>0.63649</td>
<td>0.12033</td>
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<tr>
<td>O₁</td>
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<td>0.30437</td>
<td>0.16474</td>
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<tr>
<td>O₃</td>
<td>8f</td>
<td>0.32289</td>
<td>0.54153</td>
<td>0.11905</td>
<td>1.00</td>
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</table>

Space group: C2/c (monoclinic)—unit cell parameters: \(a = 5.1704 \text{Å}, \ b = 8.9183 \text{Å}, \ c = 10.1797 \text{Å}, \ \beta = 91.28^\circ\). Cell volume: 469.28 Å³. Reliability factors—Rp: 11.6%, Rwp: 11.6%, Rexp: 7.39%.

are five coordinated by five oxygen atoms with various of Fe–O bond lengths (around 2 Å), forming distorted FeO₅ hexahedron. In this structure Fe atoms occupy approximately central positions within the FeO₅ hexahedron, and each FeO₅ hexahedron shares two edges with adjacent hexahedrons to form edge-shared FeO₅ hexahedrons single chains, and this chains extend along the [−1,0,1] direction to form a series of infinitely long chains (see Fig. 3). The B–O distance varies from 1.1488 Å to 1.6346 Å with an average value of 1.4276 Å. The adjacent chains are connected by BO₃ triangles through corners. In the BO₃ plane triangle, the B atoms are not located at the central positions of the triangle. Li atoms occupy statistically two close positions with the occupancy of 50% for Li₁ and 50% for Li₂, respectively and the distance between Li₁ and Li₂ is 0.6261 Å. All the Li atoms are surrounded by three adjacent FeO₅ hexahedrons long chains connected by BO₃ triangles and arranged along those long chains. The main interatomic distances are listed in Table 2.

Fig. 4 shows the typical charge and discharge curves of LiFeBO₃ cell in the voltage range between 1 V and 4.8 V at different current density. For LiFeBO₃, an approximately analogous charge/discharge profiles can be obtained at various current densities. From Fig. 4 we can see that at a lower current density (less than 10 mA/g) the discharge curves contain an approximate flat discharge profile at 2.3 V, which is in good agreement with the redox potential in cyclic voltamograms (see Fig. 5). According to Goodenough’s report, lithium insertion into α-Fe₂O₃ (reduction of Fe³⁺ to Fe²⁺) redox couple occurs near 1 V versus Li⁺/Li [7], considering the fact that the Fe³⁺/Fe²⁺ reduction potential is near 3.5 V for phosphor–olivine.

Table 2
Selected interatomic distances (Å) in LiFeBO₃

<table>
<thead>
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<th>Selected atoms</th>
<th>Distances (Å)</th>
<th>Selected atoms</th>
<th>Distances (Å)</th>
</tr>
</thead>
<tbody>
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<td>1.9977</td>
<td>Fe₂–O₁</td>
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</tr>
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<td>2.3573</td>
<td>Fe₂–O₁</td>
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<td>Fe₁–O average</td>
<td>2.0967</td>
<td>Fe₂–O average</td>
<td>1.9653</td>
</tr>
<tr>
<td>B–O₁</td>
<td>1.4993</td>
<td>Fe₁–Fe₂</td>
<td>0.3269</td>
</tr>
<tr>
<td>B–O₂</td>
<td>1.6346</td>
<td>Li₁–Li₂</td>
<td>0.6261</td>
</tr>
<tr>
<td>B–O average</td>
<td>1.4276</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Perspective view of both FeO₅ hexahedron and the chains of FeO₅ hexahedrons running along [−1,0,1].
LiFePO$_4$ reflecting an inductive effect of the polyatomic, which lowers the energy of the transition metal redox couple in the phosphate-based cathode with respect to the Fermi level of lithium. We believe that the relatively high discharge plateau voltage observed in our work than that of α-Fe$_2$O$_3$ suggests an inductive effect of the BO$_3$ group. However, at a higher current density (50 mA/g) a lower discharge plat voltage and capacity loss can be observed in Fig. 4. The decrease of plat voltage and capacity at higher current density may be due to low electric conductivity and/or lithium diffusivity in LiFeBO$_3$. Despite this, LiFeBO$_3$ shows a good electrochemical property. As shown in Fig. 4, an initial discharge capacity around 125.8 mAh/g can be obtained at the discharge current density of 5 mA/g. Even when the discharge current density is increased to 50 mA/g, a specific capacity of 88.6 mAh/g can still be held, which is far higher than that of about 8.8 mAh/g reported by Legagneur et al. Comparing with LiFePO$_4$ synthesized by different materials and/or different synthesis routes show an obvious different electrochemical performance [16,17], it is reasonable to think that the difference of the electrochemical performance between Legagneur et al.’s and us may be due to the different experimental method, which including different reactants, different mixed method for precursors, different protect atmosphere, and different react temperature. It has been reported that for lithium borate the experimental result is very sensitive to the synthesized technique [18]. It should be noticed that in Fig. 4 the charge curve proceeds at much higher potentials than discharge curve. The mechanism is still open and the further studies should be made in the future.

The cycle performances and coulombic efficiency of the LiFeBO$_3$ cell obtained in our experiment are shown in Fig. 5. The cells were charged/discharge at 5 mA/g in the 1.0–4.8 V range versus Li$^+$/Li and the initial discharge capacities of 125.8 mAh/g can be obtained. The mean fade of capacity is only 0.3% per cycle except for the first cycle. The coulombic efficiency was calculated from the capacity ratio of discharge and charge in each cycle. As shown in Fig. 6, the coulombic efficiency of near to 100% was realized except for the first cycle. The good coulombic efficiency suggests that LiFeBO$_3$ can be used as reversible insertion materials. However, it should be noticed that the relatively good performance is achieved in a wide potential window (charge/discharge between 1 V and 4.8 V), which is too large for real applications and the data on the performance for the more realistic values of potential window (e.g. between 4 V and 2.5 V vs. lithium) is needed in the future work.

In order to further improve the electrochemical perform of this material, carbon-coated LiFeBO$_3$ compounds (named as C-LiFeBO$_3$) were synthesized. Fig. 7 shows the XRD pattern of the C-LiFeBO$_3$ compounds prepared by solid-state reaction at 650 °C. For comparison, the XRD pattern of the pure LiFeBO$_3$ is also shown at the bottom of Fig. 7. The diffraction pattern of the C-LiFeBO$_3$ can be indexed as a monoclinic lattice system (space group C2/c) which is consistent with that of pure LiFeBO$_3$. No evidences for crystalline carbon or amorphous peak can be observed in Fig. 7. The exact amount of carbon coated on the LiFeBO$_3$ sample was determined by using thermal analysis experiment method [19]. The TG and DTA curves of carbon gel under air flow are shown in Fig. 8. The only one
Fig. 7. X-ray diffraction patterns of LiFeBO₃ sintered at 650 °C: (a) carbon-coated C-LiFeBO₃ and (b) pure LiFeBO₃.

Fig. 8. The TG and DTA curves of carbon gel under air flow.

Fig. 9. The TGA curves of both LiFeBO₃ and carbon-coated C-LiFeBO₃ under air flow: (a) LiFeBO₃ and (b) C-LiFeBO₃.

A comparison of the discharge capacity as a function of cycle number for LiFeBO₃ and carbon-coated C-LiFeBO₃ (black powder) is given in Fig. 10. The samples were cycled between 1.0 V and 4.8 V at different current density (5 mA/g, 10 mA/g, 20 mA/g, 50 mA/g). The discharge capacity of C-LiFeBO₃ is larger than that of pure LiFeBO₃ at all current density. In the case of 5 mA/g, the initial discharge capacity is 158.3 mAh/g, which is 72% of theoretical capacity, and the pure LiFeBO₃ gives 57% of theoretical capacity around 125.8 mAh/g at this current density. When the current density is increased to 50 mA/g, the initial discharge capacity of 122.9 mAh/g for C-LiFeBO₃ can be obtained, which is higher than the value of 88.6 mAh/g for pure LiFeBO₃. This confirms that the addition of carbon black during the synthesis of LiFeBO₃ can improve the electrochemical performance of the material in terms of practical capacity and charge–discharge rate.

In order to explain why the carbon-coated C-LiFeBO₃ has the better electrochemical performance, the SEM images are shown in Fig. 11(a) and (b) for comparison. From SEM image shown in Fig. 11(a), we can see that the particles of uncoated LiFeBO₃
sample are agglomerated severely with the particle size around 1.5 \( \mu \text{m} \), which is larger than that of carbon-coated LiFeBO\(_3\) sample and thus, has a relative smaller surface area than that of carbon-coated LiFeBO\(_3\). According to Padhi’s report [20], the surface area of the sample is a critical factor in determining the electrochemical performance. The charge–discharge process is controlled by lithium transport across two phases interface, and therefore, the better electrochemical performance of carbon-coated LiFeBO\(_3\) is mainly due to the small particles size. In addition, from Fig. 11(b) we can see that the carbon-coated method can prevent the particle from agglomerating and carbon particles can be dispersed uniformly between LiFeBO\(_3\) particles and thus, the electronic conductivity between LiFeBO\(_3\) particles can be enhanced.

4. Conclusions

In this paper, LiFeBO\(_3\) cathode material has been synthesized successfully by the solid-state reaction using Li\(_2\)CO\(_3\), H\(_3\)BO\(_3\) and FeC\(_2\)O\(_4\)·2H\(_2\)O as starting materials. The Rietveld refinement results show that the single-phase LiFeBO\(_3\) with monoclinic structure can be obtained in our experimental process. Electrochemical test shows that the LiFeBO\(_3\) exhibits better electrochemical properties. At the discharge current density of 5 mA/g an initial discharge capacity around 125.8 mAh/g can be obtained. Even when the discharge current density is increased to 50 mA/g, specific capacity of 88.6 mAh/g can still be held. The cycle performance shows that LiFeBO\(_3\) exhibits a better cycle stability. At the current density of 5 mA/g the mean fade of capacity is 0.3% per cycle except for the first cycle. The coulombic efficiency of close to 100% are realized. In order to improve the electrochemical properties, the carbon-coated LiFeBO\(_3\), C-LiFeBO\(_3\), are also prepared. The amount of carbon around 5% was obtained by TGA technique. A higher discharge capacity, 158.3 mAh/g at 5 mA/g and 122.9 mAh/g at 50 mA/g, was obtained for C-LiFeBO\(_3\). Combined with its better electrochemical properties and low-cost raw materials, LiFeBO\(_3\) may be used as the cathode materials for lithium-ion batteries.

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References


