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Reversible lithium intercalation in amorphous iron borate

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Abstract Upon electrochemical reduction in a lithium cell, calcite-type FeBO_3 gives an amorphous compound which can intercalate 3 Li per formula at 1.1 V, ending with metallic iron for full discharge to 0.9 V. The amorphous phase can be cycled reversibly at 1.5–3 V with capacities as high as 300 Ah/kg. This material was successfully tested as an inexpensive negative electrode for Li-ion batteries with LiCoO_2 as the positive electrode. Its behaviour is quite different from that of Fe_2O_3 , both in intercalation potential and cyclability.

Keywords Lithium batteries · Iron · Borate

Introduction

Electrode materials for lithium batteries must meet a number of requirements which are difficult to satisfy simultaneously. These concern primarily potential and capacity, but also the cost of the raw material, the ease of production and the absence of toxicity. None of the main oxides studied or commercialized for lithium batteries, based on cobalt, nickel or manganese, meet all these conditions. Iron is a very interesting element from the point of view of cost and environmental impact. However, the potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple vs. Li/Li^+ is inherently low in simple oxides [1, 2]. Several directions have been investigated to improve the performances of iron-based oxides for lithium batteries: (1) using higher Fe oxidation states, as in the so-called “super-iron” battery [3], (2) changing the $\text{Fe}^{3+}/\text{Fe}^{2+}$

potential by varying the covalency of the X-O bond in compounds containing $(\text{XO}_x)^{n-}$ oxoanions [4, 5]. A drawback of these routes is the necessary inclusion of additional elements such as potassium or barium (in super-iron batteries), phosphorus or sulfur (in oxoanionic compounds). These increase considerably the molar mass, hence decrease the specific capacity at a given lithium intercalation range.

We present here a study of the lithium intercalation properties of iron borate, FeBO_3 . This compound is not a good candidate a priori for lithium intercalation, because it crystallizes with the calcite structure, which does not contain empty sites for intercalation reactions [6]. We will show, however, that FeBO_3 yields on first discharge an amorphous phase that can be cycled with high reversibility at low potential. Li-ion batteries based on FeBO_3 and LiCoO_2 were built and tested successfully. This compound is interesting in many ways: both iron and boron are non-toxic and abundant; the preparation of iron borate is simple; and boron is a light element, resulting in a theoretical capacity of 234 Ah/kg for each lithium exchanged per FeBO_3 formula unit.

This system has not been studied previously, to our knowledge. However, we became aware at the time of submitting this paper of a similar study by Gaubicher et al. [7], which confirmed our results and extended them to another very interesting iron borate, Fe_3BO_6 .

Experimental

FeBO_3 was prepared by a solid state reaction between Fe_2O_3 and H_3BO_3 in the appropriate stoichiometric ratio at 860 °C [8]. LiCoO_2 was obtained by co-decomposition of the carbonates at 800 °C.

Samples were characterized by X-ray diffraction using a Siemens D-5000 diffractometer equipped with Cu K α radiation. Electrochemical tests were carried out in a liquid electrolyte at room temperature using Swagelok cells. The electrolyte was a 1 M solution of LiPF_6 in ethylene carbonate-dimethoxyethane (1:2). For initial studies versus metallic lithium, positive electrodes were cut from a paste made of an intimate mixture of active material, carbon black (Y50A grade, SNNA, Berre, France) and PTFE

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(Aldrich) in weight ratio 70:20:10, and dried at 120 °C under vacuum. Quantities used in the cells were in the range 20–35 mg/cm² active material. Negative electrodes were cut from 200 μm-thick lithium foil (Metall, Germany). Cells were assembled in a glove box under argon with ≤ 1 ppm H₂O. Additional Li-ion cells were mounted with FeBO₃ pellets as the negative and LiCoO₂ as the positive electrode, and assembled either in Swagelok or in all-plastic sealed bags [9]. Electrochemical studies were carried out using a MacPile Controller (Bio-Logic, Claix, France), in either galvanostatic mode or by step-potential electrochemical spectroscopy (SPES) [10], using typically 10 mV/h steps. All electrochemical tests were carried out at room temperature. X-ray powder diagrams were recorded on positive pellets after disassembling cells stopped at specific points on the cycling curves.

Results

The FeBO₃ obtained contains minor amounts of residual Fe₂O₃ (ca. 8% from Reitveld refinement, see Fig. 1, top); this impurity could not be eliminated by using starting mixtures richer in boron; it had no significant effect on the electrochemical behavior. The XRD pattern of LiCoO₂ was fully consistent with the known structure of this compound (rhombohedral NaFeO₂-type structure [11]).

A SPES voltammogram on a FeBO₃-Li battery and the corresponding discharge-charge curve vs. $x(\text{Li})$ are shown in Fig. 2. Unexpectedly, the first discharge yields a very long and flat plateau at 1.0 V, with no visible kink at $x(\text{Li}) = 1$, which would correspond to the quantitative reduction to Fe²⁺. This voltage plateau proceeds all the way to $x(\text{Li}) = 2.64$. Subsequent galvanostatic cyclings on batteries with lower cathodic mass confirmed that this plateau actually extends to $x = 3$, i.e. to a complete reduction to metallic iron (see Fig. 3). The associated capacity is very high (701 Ah/kg for $x = 3$).

On charge, the behavior is completely different. Lithium extraction occurs along a broad oxidation peak centered around 2.10 V (Fig. 2a), corresponding to an S-shaped

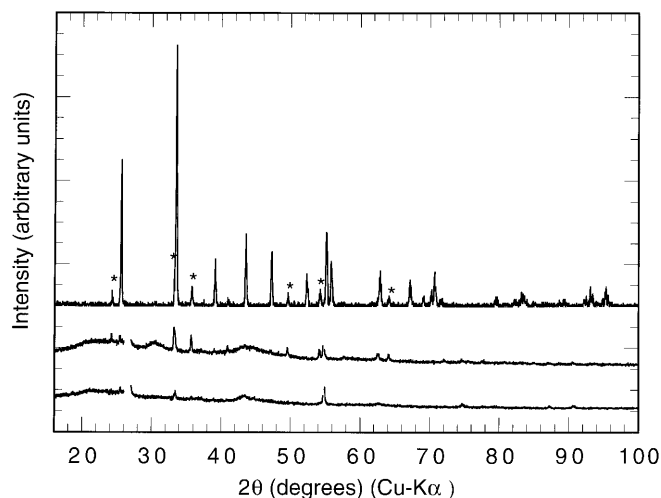


Fig. 1 X-ray powder diagrams of FeBO₃ initially (top), after full discharge (middle) and after recharge (bottom). The main reflections of Fe₂O₃ are indicated by asterisks

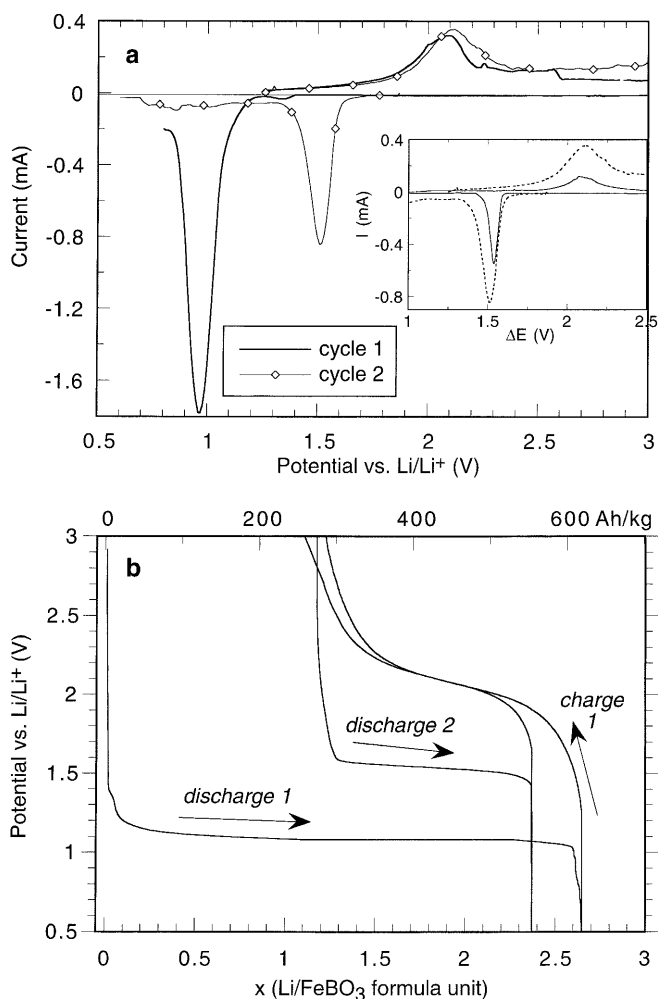


Fig. 2 SPES of FeBO₃-Li batteries at 20 mV/h: **a** voltammogram and **b** charge-discharge curve (two full cycles shown). Inset: detail of second cycle at different potential step sweep rates. Full line: 5 mV/h; dashed line: 20 mV/h

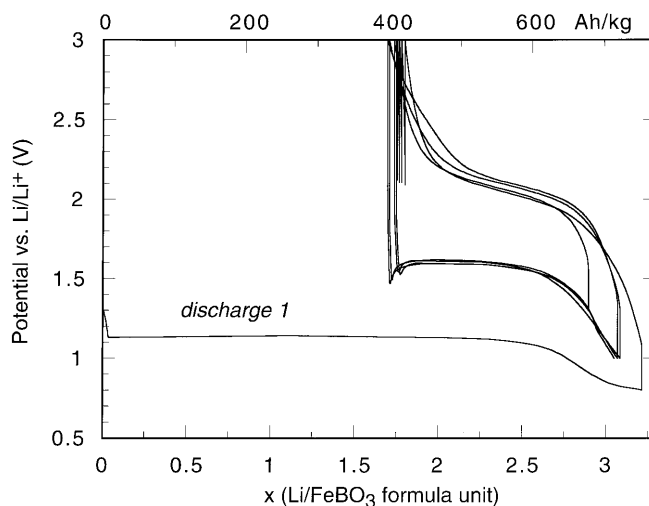


Fig. 3 Galvanostatic cycling of a FeBO₃-Li battery at C/20 rate

curve in $U=f[x(\text{Li})]$ (Fig. 2b). The recovered capacity is ca. 300 Ah/kg up to 3.0 V cut-off for the first charge.

Further cycles give a very constant, reversible behavior with some peculiarities (see Fig. 2): (1) the peak shape is very different between discharge (sharp reduction peak) and charge (broad oxidation peak); (2) there is an important potential difference between these two reactions, which are centered around 1.5 V on discharge and 2.1 V on charge. Subsequent X-ray patterns taken on positive pellets extracted from batteries after full discharge and first recharge show that the compound becomes disordered during the first discharge and remains amorphous on cycling (see Fig. 1). However, the X-ray pattern of the positive pellet after the first discharge (Fig. 1, middle) still shows the Fe_2O_3 reflections, confirming that a selective reduction and amorphization of FeBO_3 , but not of the Fe_2O_3 fraction, took place in the lithium cell.

A comparison of SPES carried out at different sweep rates (see Fig. 2a, inset) shows that the reduction and oxidation potentials do not depend on the sweep rate, so that the difference between charge and discharge current peaks is not due to kinetics. Interestingly, the reduction and oxidation exhibit classical features of two-phase and single-phase reactions, respectively [12].

The behavior observed in slow-step voltammetry is fully confirmed by galvanostatic measurements. Figure 3 shows the first five cycles of a FeBO_3/Li battery cycled at $C/20$ rate. The first, long discharge plateau is observed at 1.13 ± 0.02 V; the potential and capacity ranges for subsequent cyclings on the amorphous phase are confirmed. The evolution of the capacity with cycle number is shown in Fig. 4. Although the capacity decreases significantly after eight cycles, it is interesting to note that capacities in excess of 200 Ah/kg are measured up to cycle 14.

The average discharge potential of the amorphous phase (1.5 V) makes it an interesting material to test as a

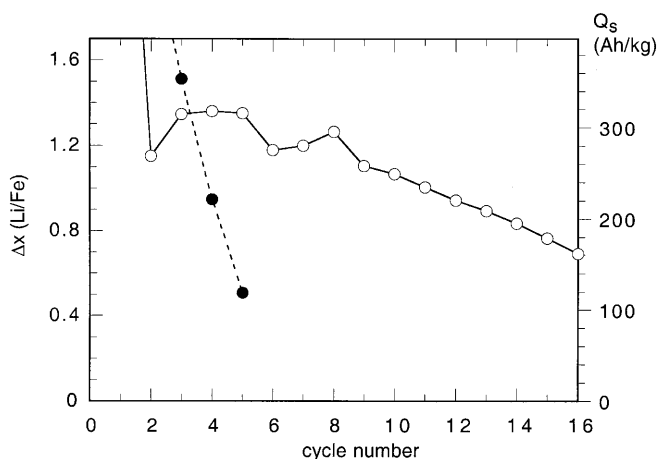


Fig. 4 Evolution of the capacity of $\text{FeBO}_3\text{-Li}$ and $\text{Fe}_2\text{O}_3\text{-Li}$ batteries with cycle number ($C/20$ rate). *Open circles*: FeBO_3 ; *closed circles*: Fe_2O_3 . Q_s = specific capacity (molar mass-dependent scale, applicable to FeBO_3 only)

negative electrode in Li-ion batteries, compared to other low-potential oxides [13]. Several test cells with a FeBO_3 negative and a LiCoO_2 positive electrode have been cycled. The results (see Fig. 5) are in agreement with the potential observed vs. Li/Li^+ : after an initial charge at 3.0–3.5 V, such batteries deliver ca. 300 Ah/kg (with respect to FeBO_3 mass) on discharge in the potential range 3.5–1 V (200 Ah/kg between 3 and 2 V).

Discussion

The absence of any particular feature for Fe^{2+} is rather surprising. In fact, a battery initially programmed to stop on discharge at $x = 1.1$ (i.e. with iron oxidation state close to +2) and recharged from that point actually

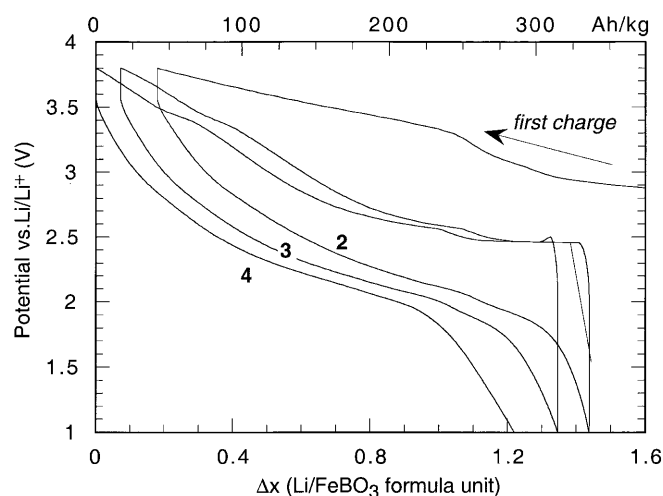


Fig. 5 Cycling of a Li-ion battery $\text{LiCoO}_2\text{-FeBO}_3$ at $C/20$ rate. Cycle numbers are indicated. Capacities are expressed with respect to FeBO_3

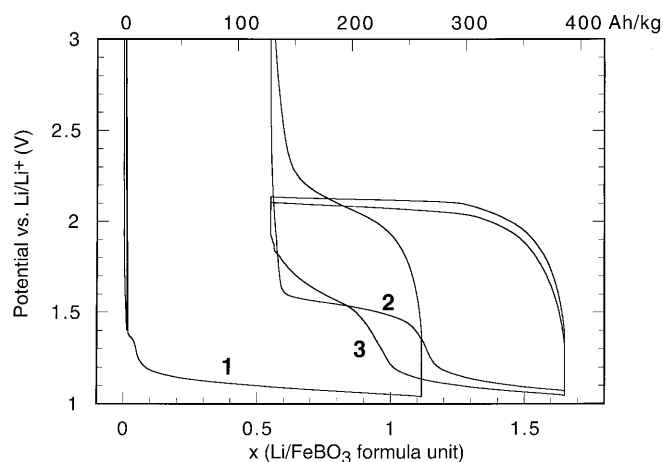


Fig. 6 Charge-discharge curve of a $\text{FeBO}_3\text{-Li}$ battery with $\Delta x(\text{Li}) \leq 1.1$ under potentiostatic control at 5 mV/h (discharge numbers are indicated)

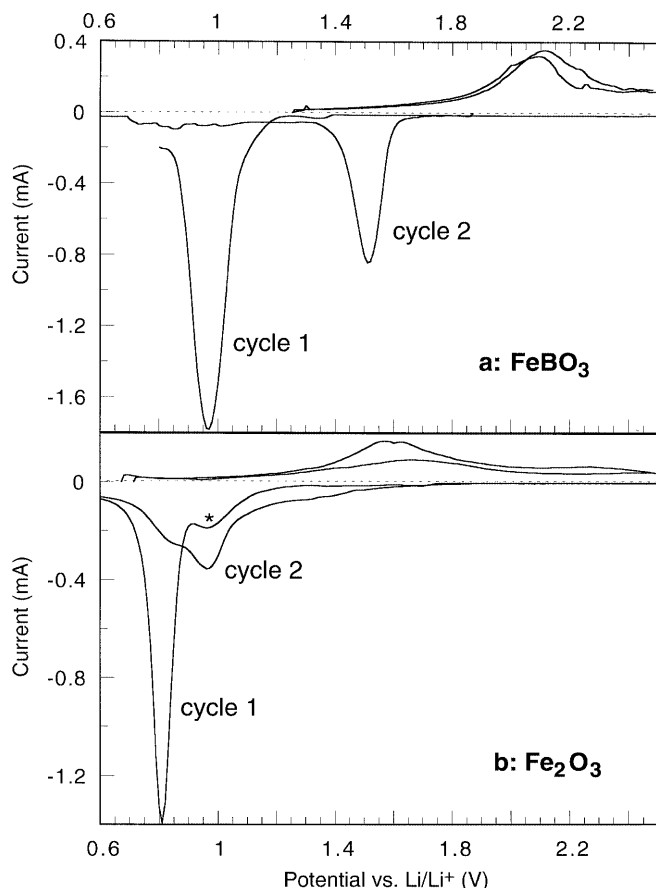


Fig. 7 Compared SPES of FeBO_3 (a) and Fe_2O_3 (b) vs. Li at 20 mV/h (first two cycles). The first reduction peak of Fe_2O_3 is marked by an asterisk

behaves much like those discharged all the way to metallic iron (compare Figs. 2b and 6). The second discharge in Fig. 6 shows a double plateau which can be explained as follows: (1) at 1.5 V, lithium is intercalated in the amorphous phase already formed on first discharge; (2) at lower potential (ca. 1.1 V), we observe the continuation of the initial reducing amorphization of iron borate. The important conclusion is that the amorphous phase starts to form from the very beginning of FeBO_3 reduction on the 1.1 V plateau.

The potentials observed on cycling FeBO_3 vs. lithium are much lower than those observed for other iron oxoanionic compounds, such as the $\text{Li}_x\text{Fe}_2(\text{XO}_4)_3$ series ($\text{X}=\text{P}, \text{W}, \text{S}$) [5], although boron is only slightly less electronegative than phosphorus. However, this comparison is of limited use, since no actual lithium intercalation takes place in the FeBO_3 structure. We observe instead a phase transformation occurring at a constant potential of ~ 1.1 V. This behavior resembles that recently reported for simple oxides MO ($\text{M}=\text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) when cycled vs. lithium between the M^{2+} and M^0 oxidation states, which all give on first discharge an amorphous or nanocrystalline phase which can be cycled at low potential vs. Li [13].

In order to check whether FeBO_3 does not simply transform into an amorphous Fe/FeO_x system, we compared the electrochemical behavior of FeBO_3 with that of $\alpha\text{-Fe}_2\text{O}_3$ in cells assembled and cycled under the same conditions. The results (see Fig. 7) show important differences between these two electrochemical systems: (1) the potentials are markedly different – and systematically lower for Fe_2O_3 – on both reduction and oxidation, even after amorphization (cycle 2); (2) the reduction of Fe_2O_3 is actually a two-step reaction with a first, smaller peak corresponding to the $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ reaction, as reported previously [1] (see asterisk in Fig. 7b). As already noted, no such feature is observed for FeBO_3 . On the other hand, both systems show a similar difference in shape between reduction (sharp peaks) and oxidation (much broader peaks 500–600 mV higher in potential).

Regarding cyclability, the comparison between FeBO_3 and Fe_2O_3 (see Fig. 4) shows that the former presents a much better capacity retention. This further confirms that the phase formed on first reduction is different for these two initial materials.

Conclusions

We showed in this study that the reduction of calcite-type FeBO_3 yields an interesting amorphous phase, which can be cycled reversibly in lithium batteries and gives a very flat discharge at 1.13 V vs. Li/Li^+ . As a result, capacities as high as 200 Ah/kg were obtained after 14 cycles. The amorphous phase formed behaves differently and better than Fe_2O_3 on cycling. However, further work is needed to optimize cycling and reduce the capacity drop on cycling.

Subsequent studies by X-ray absorption and Mössbauer spectroscopy are under way to gain a better understanding of the evolution of the iron oxidation state and structure on electrochemical cycling of FeBO_3 .

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