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The effect of the reactive milling of graphite with boron nitride, tin and antimony on lithium insertion

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Boron-, tin-, and antimony-based graphite composites were studied as potential materials for negative electrodes in lithium-ion batteries. The materials were prepared by the reactive milling of mixtures of graphite (90 wt. %) with boron nitride (10 wt. %), tin (10 wt. %), or antimony (10 wt. %). Milling was performed for 2 h, 4 h, 6 h, or 8 h. The composites were characterized by X-ray diffraction and nitrogen adsorption at 77 K (BET). A gradual development of surface area during milling was observed as well as the appearance of amorphous forms. The galvanostatic characteristics of lithium insertion–deinsertion for these new composite materials were investigated. Graphite-tin composites exhibit the best reversible capacity. Modification by milling leads to a significant particle size reduction, good association of the metallic phase with graphite crystal grains, and consequently to an increase of the reversible capacity. A significant enhancement of the irreversible capacity for the composites is also observed due to the development of specific surface area.

Key words: *lithium-ion cell; graphite; milling; anodic material*

1. Introduction

Graphite remains the most often used anode material for lithium-ion accumulators. Li-ion cells with graphite anodes are characterized by long durability (over 1000 cycles), high stable voltage (>3 V), a lack of hysteresis (i.e., the divergence between the polarization of lithium insertion and deinsertion). The maximum reversible capacity for lithium intercalation into graphite is 372 mAh/g (the 1st stage of the intercalation compound Li_xC_6, where $x = 1$) and is related to the graphitic crystal structure [1–3]. The irreversible capacity, i.e. the amount of lithium consumed in the formation of solid electrolyte interphase (SEI) during the first cycle is very low, ca. 50 mAh/g. The

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great interest for graphite as the Li-ion anode is also caused by moderate price of both natural and synthetic graphite. Due to all these useful characteristics, a lot of research has been devoted to the further modification of graphite in order to increase the reversible capacity through the insertion and deposition of heteroatoms, metals, and other treatments.

Among various modifications of graphitic materials for Li-ion cells, structural changes through mechanical treatment [4–6], incorporation of heteroatoms [7–12], and a carbon surface coating by pyrolytic carbon, metals [11–16] have already been proposed.

Even if it is assumed that doping with heteroatoms, e.g. boron [8], is beneficial for the process of lithium ion intercalation into graphites, practical results show some discrepancies [10]. When a shell of BC_x covers the graphite surface, its properties should be significantly improved, because B incorporated into the structure of a carbonaceous material reduces its reactivity through changes in charge distribution in the crystallographic plane, especially on the edges [7]. This hinders the processes of surface chemical degradation [9], which directly affects the prolongation of electrode lifetime during cycling. The expected improvement of lithium storage capability for boronated carbons seems to be due to the electron deficiency of boron, which has only three valence electrons. This electron acceptor character of boronated carbon can increase Li–C binding energy. On the other hand, when boron occurs in the form of boron carbide, the irreversible capacity rises, because this compound does not take part in the process of lithium storage [7].

One of alternatives for graphite anodes are materials made of the metal–carbon composites having high capacities in the process of forming intermetallic compounds with lithium, e.g. tin $Li_{22}Sn_5$ and antimony Li_3Sb [7, 11–14]. Unfortunately, apart from the capacity, which can be three times higher than that of graphite, their greatest disadvantage is a poor cycle life, usually not exceeding a few cycles. This is due to the fact that during the creation of compounds with lithium, the system volume increases more than three times, and during the reverse process it returns to the starting volume, thus causing mechanical stress, particle fracture, and a loosening of the electrical contact between them.

In the present work, attempts were performed to incorporate boron atoms into graphite structure, using high-energy ball-milling. Trials were also undertaken to combine the positive features of graphite with such metals as Sn and Sb by forming graphite–metal composites through milling.

2. Experimental

Graphite–boron composites were synthesized by high-energy ball milling using a shaker-type ball mill Retsch MM 200. Graphite UF2 of high purity from Kropfmühl (Germany) was used. Mixtures of graphite 90 wt. % and boron nitride 10 wt. % were put into the mill reactor together with the grinding balls. The weight ratio of the grinding balls to the milled material was 5:1. Both the reactor and grinding balls were made of zirconium oxide. The milling was conducted in an inert argon atmosphere. Mixtures of graphite and BN were milled for 2, 4, 6, and 8 hours and the obtained materials were designated as 10B2h, 10B4h, 10B6h, and 10B8h, respectively. Sn–graphite and Sb–graphite composites were obtained and labelled analogously (Sn–graphite composites: 10Sn2h, 10Sn4h, 10Sn6h, and 10Sn8h, and Sb–graphite composites: 10Sb2h, 10Sb4h, 10Sb6h, and 10Sb8h).

Physicochemical characterization of the obtained materials was conducted using X-ray diffraction (XRD) and nitrogen adsorption at 77 K (BET). XRD measurements were done using a Phillips PW 1710 diffractometer with FeK_α radiation, whereas for nitrogen adsorption an ASAP 2010 (Micromeritics) analyser was used.

Galvanostatic characteristics were determined using Atlas-Sollich galvanostats 9835 in two-electrode Swagelok cells. The anodes in the half-cells were round pellets cut out from copper foil covered with a mixture of the examined composite: binder (10 wt. % of PVdF) and acetylene black (5 wt. %). The counter electrode (and simultaneously the reference electrode) was metallic lithium. The electrolyte was a 1 M solution of $LiPF_6$ in a 1:1 mixture of ethylene carbonate and diethyl carbonate. The half-cells were cycled between 0 V and 2 V using a constant current density of 10 mA per gram of active material.

3. Results and discussion

The results of all physicochemical and electrochemical tests for the composites are collected in Table 1.

Table 1. Physicochemical and electrochemical results for the milled composites

Sample	BET surface area [m^2/g]	Irreversible capacity (x)	Reversible capacity (x)
Graphite	14	0.28	1.00
10B2h	162	1.20	0.85
10B4h	212	1.36	0.96
10B6h	304	2.00	0.92
10B8h	-	2.19	0.91
10Sn2h	153	1.39	1.19
10Sn4h	241	1.83	1.27
10Sn6h	322	2.20	1.31
10Sn8h	324	2.21	1.36
10Sb2h	153	1.44	1.14
10Sb4h	233	1.93	1.17
10Sb6h	280	2.34	1.22
10Sb8h	301	2.39	1.34

For $x = 1$, the first stage of the intercalation compound Li_xC_6 is formed.

Milling causes a significant development of surface area evidenced by adsorption isotherms. Both surface area and the ratio of micropores to the total porosity of materials rise. Figure 1 presents typical adsorption isotherms for selected composites of graphite with B, Sn, and Sb milled for 2 h, 6 h, or 8 h.

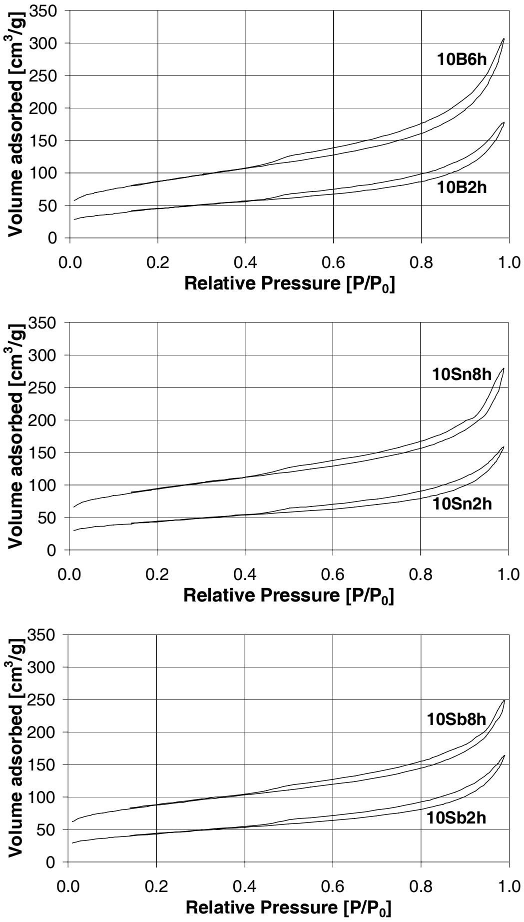

Fig. 1. Nitrogen adsorption isotherms for the graphitic composites 10B2h and 10B6h, 10Sn2h and 10Sn8h, and 10Sb2h and 10Sb8h

As can be seen, even two hours of milling results in a surface area increase by an order of magnitude compared to pure graphite (Table 1). A longer milling causes even greater surface development, however not so distinct. This effect is observed for all the milled materials being connected with the applied modification technique. High-energy milling not only links the mixture components into a composite material, but also causes grinding of particles and an increase in the surface area. The materials undergo structure degradation and become amorphous. Another effect of milling is the increasing number of active sites and dangling bonds [16].

A strong degradation of the crystal structure after milling is clearly evidenced by the XRD patterns as a broadening and disappearing of certain signals. Selected XRD patterns are shown in Fig. 2.

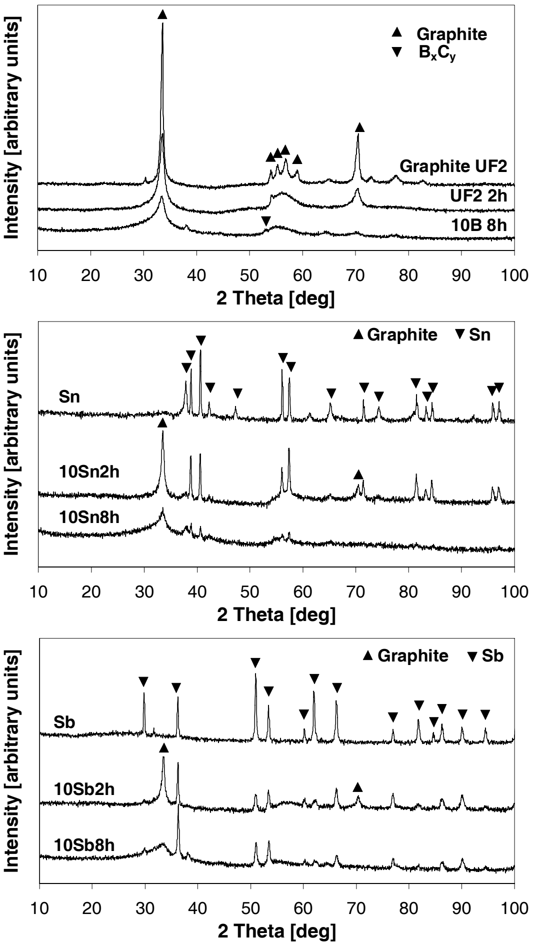

Fig. 2. Selected XRD patterns for the following pairs of composite materials: graphite and 10B8h, 10Sn2h and 10Sn8h, and 10Sb2h and 10Sb8h

In the case of 10Sn and 10Sb there are no signs of XRD peaks from any intermediate compounds of mixture components that could be formed during milling. On the other hand, in the case of 10B8h there is a signal in the XRD pattern that might be ascribed to the intermediate phase of some compound of carbon and boron (B_xC_y). However, such an assumption should be supported by further examinations with a longer milling time. In the hypothesis that boron forms a compound with carbon, the residual nitrogen from boron nitride can eventually create nitrogen functionalities with carbon.

Physicochemical results are fully confirmed by the data from galvanostatic experiments, which were done in half-cells with metallic lithium as both the counter and reference electrode (Fig. 3). For comparison, the galvanostatic intercalation–deintercalation process with a pure UF2 graphite sample is also presented. For all composites an increase of irreversible capacities can be seen, which is due to the development of surface and the creation of a large number of active sites, such as crystal structure defects and dangling bonds. Larger hysteresis in the charge–discharge curves indicates that the structure has been disordered to a large extent and that graphitic regions coexist with amorphous ones. It also proves that different sites of various Li–C bonding exist in composites where the deinsertion process involves higher energies.

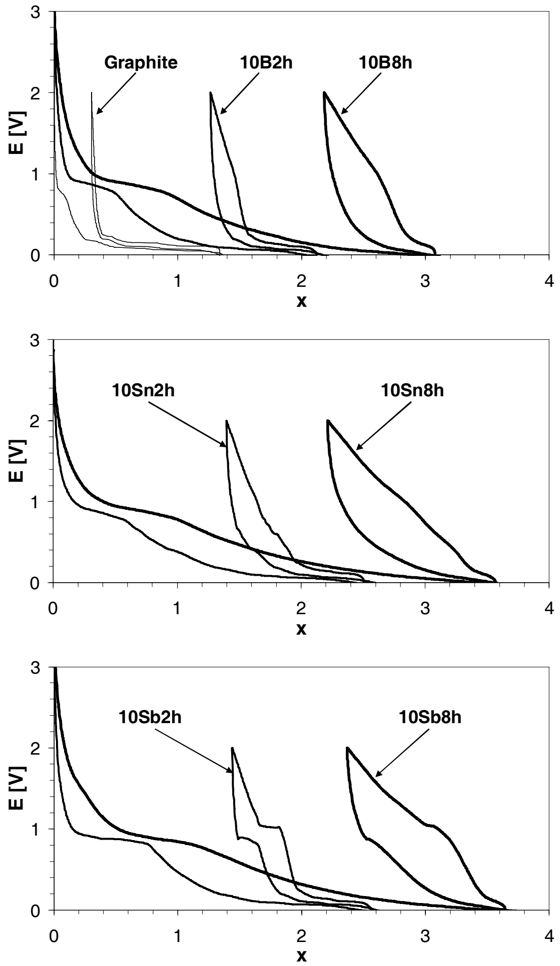

Fig. 3. Galvanostatic curves of lithium insertion–deinsertion for graphite and the following composite materials: 10B2h and 10B8h, 10Sn2h and 10Sn8h, and 10Sb2h and 10Sb8h

Three small plateaus are visible in the discharge curve of 10Sn2h in the range of 0.55–0.85 V vs. Li/Li$^+$ (Fig. 4). They are connected with lithium ion deinsertion from the intermetallic compound Li$_x$Sn$_y$. It is noteworthy that these plateaus are very reproducible and observed in repeated experiments. Upon grinding, tin becomes more amorphous, which is the reason why the plateaus disappear in the composite 10Sn8h.

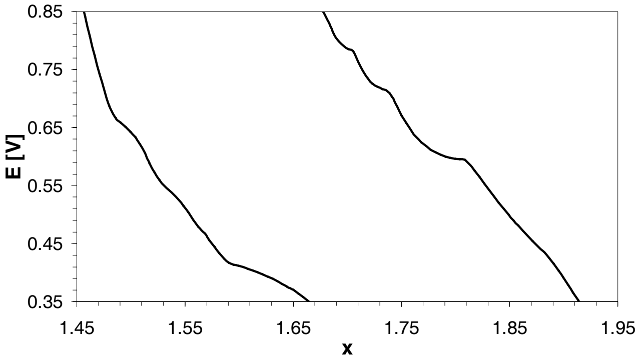

Fig. 4. Plateaus in the composite 10Sn2h
(left: lithium insertion; right: lithium deinsertion)

The situation is similar in the case of antimony–graphite composites. For the sample 10Sb2h, a distinct plateau at 1.03 V vs Li/Li$^+$ is seen on the discharge curve (Fig. 5). The plateau vanishes upon milling and is markedly smaller in sample 10Sb8h (Fig. 3).

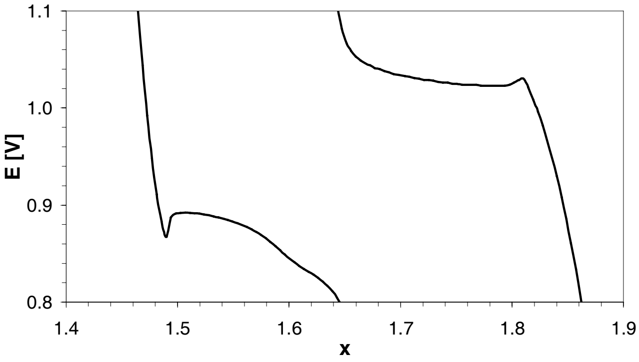

Fig. 5. Plateaus in the composite 10Sb2h
(left: lithium insertion; right: lithium deinsertion)

The galvanostatic curves obtained for composites milled with boron nitride are different in character. Materials 10B2h and 10B8h do not exhibit any plateaus beside those of graphite (in the range of 0–0.3 V), which proves that neither boron nitride nor B$_x$C$_y$ compound, created during prolonged milling, do not take part in the process of lithium storage.

4. Conclusions

The positive effect of boron on Li insertion in graphite, described in literature, has not been confirmed in the present work, in which graphite was milled with boron nitride. Nevertheless, the technique of milling can be suitable for obtaining mixtures of graphite with other boron compounds.

Milling of graphite with tin and antimony gave positive results. Upon milling, reversible lithium insertion capacity rises; unfortunately, irreversible capacities and charge–discharge hysteresis are also increased. Modification of the mixture composition as well as milling conditions, such as the environment, milling energy, or ratio of millers to the milled material, can bring about a significant improvement in the material characteristics in terms of reversible capacities without negative effects.

Further improvement of electrochemical performance of graphitic composites with incorporated heteroatoms should be connected with the suppression of volume change during lithium intercalation–deintercalation, and with good electronic conductivity of the composite as well as a limited surface area and number of active sites.

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