

Short communication

# The importance of the active surface area of graphite materials in the first lithium intercalation

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## Abstract

When lithium is intercalated into graphite in ethylene carbonate (EC) containing electrolytes, solvent co-intercalation leading to the exfoliation of the graphite structure could occur. The exfoliation can be suppressed if an efficient solid electrolyte interphase (SEI, a passivation layer) is formed. Here we study the role played by the active surface area (ASA) of graphite materials during their first electrochemical reduction. ASA (related to the presence of defects at the carbon surface) appears as a critical graphite surface parameter influencing the surface passivation mechanism and the graphite exfoliation. The ASA of TIMREX<sup>®</sup> SLX50 synthetic graphite was modified by thermal treatment in argon and air. The electrochemical performance was characterized in 1 M LiPF<sub>6</sub>, EC:DMC electrolyte and *post mortem* analyses were performed by SEM imaging. It turned out that a decrease of the graphite ASA, i.e., an increase of the graphite structural order, hinders the formation of the passivation layer and favors the exfoliation process. In contrast, the exfoliation of the same graphite can be suppressed if its ASA is increased for example by air treatment. The ASA of the graphite kinetically controls the formation of an efficient SEI film and accordingly the irreversible charge loss is much lower in the case of graphite with a high ASA value.

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## 1. Introduction

Recent worldwide interest in hybrid vehicles has accelerated the research of larger-sized rechargeable lithium-ion batteries [1]. Their use in mobile applications requires especially to improve their energy density and consequently to reduce the irreversible capacity. Graphitic carbon materials are nowadays favored as negative electrode in commercial lithium-ion batteries. During the first discharge of such a battery, a solid electrolyte interphase (SEI) is formed and acts as a passivation layer on the graphite grain surfaces. This layer is responsible for an irreversible “capacity loss” (5–30%, dependent on the type of graphite), but also serves as protection against co-intercalation

of solvent molecules into and exfoliation of the graphite [2]. Especially for the high crystalline graphite, the formation of this passivation layer is of prime importance [3–5]. Therefore, a complete understanding of the formation process of this SEI layer with the identification of the critical parameters influencing its efficiency is essential and is a prerequisite for the development of improved graphite electrode materials for advanced lithium-ion batteries.

It is now well known that the composition of the SEI layer which results from electrolyte decomposition products depends on several parameters such as the graphite type, the electrolyte composition (nature of the salt, the solvent used), and the presence of electrolyte impurities. The influence of the electrolyte system on the exfoliation process has been described in several publications [6–8]. Ethylene carbonate (EC) is known as a good film-forming solvent component in the battery electrolyte. Mixtures of EC with dimethyl carbonate (DMC) are usually chosen as electrolyte for lithium-ion cells [3] as it will be the case in this study.

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Besides the electrolyte system, the influence of the graphite characteristics has been also investigated [7,9–11]. We observed that the surface properties of a highly crystalline graphite material have a significant influence on the electrolyte decomposition and passivation mechanism during the first electrochemical lithium insertion and, thus, on the SEI layer formation and composition. We observed that the heat treatment of a highly crystalline graphite TIMREX<sup>®</sup> SLX50 at temperatures above 1200 °C in an inert gas atmosphere resulted in a significant increase of the irreversible capacity during the first electrochemical lithium insertion, attributed to an exfoliation phenomenon [7,11]. Several parameters were identified as being responsible. Among them were the surface groups' chemistry and the amount of surface defects, both parameters being related. We noted that the amount of acidic groups seems to be an important factor that influences graphite exfoliation during electrochemical lithium insertion in EC containing electrolytes [11]. Recently, we showed that, apparently, graphite particles containing single crystals with low amount of defects tend to exfoliate easier than graphite powders containing a higher amount of defects [7]. However, the characterization methods presented in the previous works do not allow quantifying the amount of defects. By using a procedure based on oxygen chemisorption developed for carbon materials, the quantification of these defects became possible [12–14]. In fact, the cumulated surface area of the different types of defects present at the carbon surface (stacking faults, single and multiple atoms, vacancies, dislocations) corresponds to what is called the 'active surface area' (ASA) which is an intrinsic characteristic of the carbon which does not depend on the nature of the organic surface groups. The ASA concept proved to be very useful to correlate the reactivity of graphitic carbons in gas and liquid environment [14]. Recently, we studied the surface passivation of the TIMREX<sup>®</sup> SLX50 graphite powder as-received and after heat treatment at 2500 °C. We observed that the heat treatment at 2500 °C which leads to a decrease of the ASA favors the graphite exfoliation. The SEI film formation was kinetically hindered at graphite surfaces with low ASA [10]. To confirm the influence of the ASA and thus the degree of structural order at the surface on the exfoliation tendency, graphites with different active surface area were prepared and electrochemically tested. The results are presented in this paper. The objective of the work was to study the formation of the SEI passivation film in regard to the ASA of the carbon and to correlate the ASA to the electrochemical behavior during the first lithium-ion intercalation.

## 2. Experimental

The synthetic graphite material TIMREX<sup>®</sup> SLX50 (TIMCAL Ltd., Bodio, Switzerland) is a typical representative of the family of highly crystalline graphite negative electrode materials which electrochemically insert lithium up to a chemical composition of LiC<sub>6</sub> (372 mAh g<sup>-1</sup>). Variation of the graphite surface characteristics can be easily obtained after thermal modifications under various gas atmosphere without significantly changing the bulk properties (especially the total surface area) and the particle size distribution of the product. For this, the

TIMREX<sup>®</sup> SLX50 graphite was heated at 1300 °C under an argon flow and maintained for 1 min or 1 h, respectively, at this temperature. After the heat treatment, the graphite sample was either cooled in an argon atmosphere until room temperature or quenched in air. The air quenching causes a slight oxidation of the carbon sample. After cooling down to room temperature, the samples are exposed to the air atmosphere. The active surface area (ASA) was determined by outgassing the sample in an elsewhere described experimental set-up at 950 °C under vacuum (10<sup>-4</sup> Pa) [14]. An initial oxygen pressure of 66.5 Pa was introduced in the reactor at 300 °C causing chemisorption of O<sub>2</sub> on the graphite surface. The O<sub>2</sub> chemisorption process over a period of 15 h at 300 °C led to the formation of surface oxide complexes at the graphite active sites area (ASA). The amount of oxygen complexes formed was determined by mass spectrometry by measuring the amount of CO and CO<sub>2</sub> resulting from the decomposition of the oxygen complexes at temperatures higher than their formation by performing a temperature-programmed desorption (TPD) step between 300 and 950 °C. Knowing the number of each moles of each gas desorbed and taking the area of an edge carbon site that chemisorbed an oxygen atom as 0.0083 nm<sup>2</sup>, the surface area occupied by chemisorbed oxygen can be determined. Detailed information can be found elsewhere [14].

The electrochemical experiments were performed with a metallic lithium counter electrode in two-electrode arrangement in standard laboratory cells as described elsewhere [11]. The lithium foil (Aldrich) and 1 M LiPF<sub>6</sub> in EC:DMC [1:1] (Ferro) were used without any further treatment. Solutions and measuring cells were prepared in a glove box filled with argon. The oxygen content was less than 1 ppm. Working electrodes were prepared by doctor-blading the SLX50 graphite with polyvinylidene fluoride (SOLEF 1015, Solvay) binder onto a copper current collector. The electrodes were vacuum dried at 120 °C and contained ca. 10 mg of graphite (their composition was 90 wt.% graphite and 10 wt.% PVDF). Galvanostatic measurements were performed at specific currents of 10 mA g<sup>-1</sup> of carbon to complete the SEI formation in the first Li<sup>+</sup> insertion cycle. After a potential of 5 mV versus Li/Li<sup>+</sup> was reached, the discharging was continued at this constant potential until the current dropped below 5 mA g<sup>-1</sup>. The charging was performed at a constant specific current of 10 mA g<sup>-1</sup> until a cut-off potential of 1.5 V versus Li/Li<sup>+</sup> was reached. All measurements were carried out at room temperature.

## 3. Results and discussion

The TPD curves of the different SLX50 samples after chemisorption of O<sub>2</sub> at 300 °C showed that the formation of CO and CO<sub>2</sub> is completed below 900 °C, as shown in Fig. 1 for the sample SLX50 treated in argon during 1 h. This indicates that the total amount of oxygen complexes formed on the active sites during the oxygen chemisorption was totally removed during the TPD. Above 800 °C, the main gas desorbed is H<sub>2</sub> resulting from structural rearrangements of the graphite, which were not completed by the heat treatment at 1300 °C in an argon atmosphere. From the total amount of CO and CO<sub>2</sub> released after

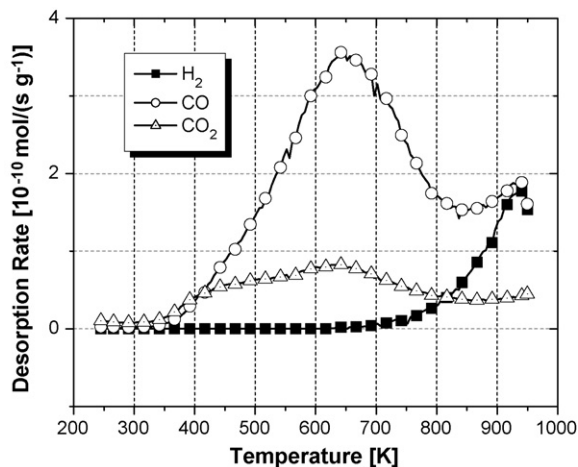


Fig. 1. Desorption rate of CO and CO<sub>2</sub> as a function of desorption temperature after oxygen chemisorption, for the "SLX50 1 h Ar" sample.

chemisorption, the ASA was calculated; the values obtained for the different SLX50 samples are reported in Table 1.

As expected, the heat treatment in argon has increased the structural ordering of the graphite and therefore removed surface defects, as seen by the decrease of the ASA values. Therefore, it is not surprising that the ASA is lower after 1 h heat treatment compared to 1 min. A subsequent air treatment leads to a mild oxidation of the graphite surface as pointed out by the increase of the ASA value after the air treatment. It must be noted that the ASA value after air quenching is higher than the value of the pristine sample indicating the presence of a higher amount of defects.

For a detailed investigation of the film formation in the first cycle, we analyzed the irreversible "charge losses" and the galvanostatic charge curves of the first lithium insertion into the graphite. The "charge losses" (irreversible capacity, in %) of the graphite samples during the first cycle are indicated in Table 1. The curves of the first galvanostatic lithium intercalation into the graphite TIMREX<sup>®</sup> SLX50 and the three heat-treated SLX50 graphite samples are reported in Fig. 2.

The pristine sample as well as the sample cooled down in air show the typical insertion properties expected for a highly crystalline graphite material. A reversible charge capacity (specific charge) of ca. 360 mAh g<sup>-1</sup> and a Coulombic efficiency of ≥90% could be observed at a specific current of 10 mA g<sup>-1</sup>.

Table 1  
Active surface area (ASA) and irreversible capacity in the first cycle of graphite materials

Graphite Sample	ASA (m <sup>2</sup> g <sup>-1</sup> )	Irreversible capacity (%), first cycle
SLX50	0.30	8
SLX50 1 h Ar	0.065	57
SLX50 1 min Ar	0.092	54
SLX50 1 h Ar + air	0.44	10

"SLX50": as-received sample; "SLX50 1 h Ar": as-received SLX50 sample treated for 1 h in an argon flow; "SLX50 1 min Ar": as-received SLX50 sample treated for 1 min in an argon flow; "SLX50 1 h Ar + air": as-received SLX50 sample treated for 1 h in an argon flow followed by an air quenching for the cooling.

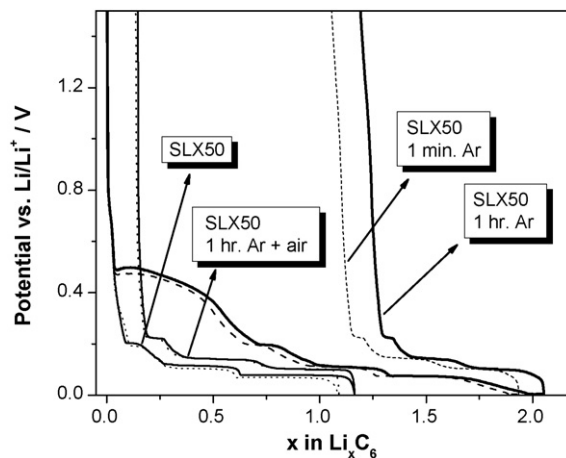


Fig. 2. First electrochemical lithium insertion into TIMREX<sup>®</sup> SLX50 (i) as received and (ii) heat-treated at 1300 °C in argon for 1 min and 1 h, respectively, and subsequently cooled down in argon and air atmosphere, respectively, in EC:DMC, 1 M LiPF<sub>6</sub> electrolyte.

No additional plateau is observed with these two samples suggesting that a protective passivation film (SEI) was formed on the graphite surface. This is confirmed by the low irreversible "charge loss" (Table 1) and the *post mortem* analyses by SEM images of the charged graphite electrodes taken from dismantled half-cells (Fig. 3). Both, the as-received SLX50 and the

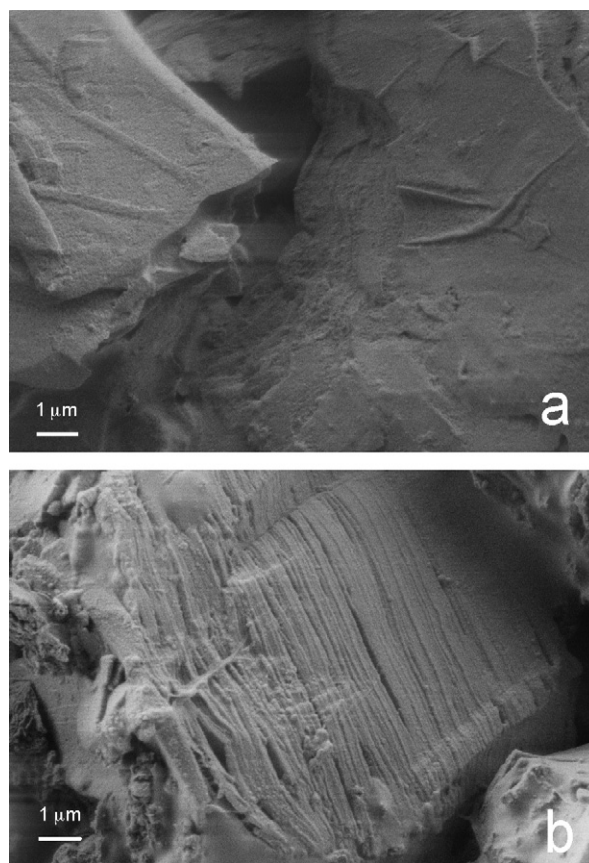


Fig. 3. SEM images of TIMREX<sup>®</sup> SLX50 graphite electrodes after the first electrochemical lithium insertion in EC:DMC, 1 M LiPF<sub>6</sub> electrolyte. (a) Commercial graphite and (b) graphite heat-treated at 1300 °C in argon for 1 h.

“SLX50 1 h Ar + air” graphite electrodes show a uniform and relatively dense film on the graphite particles. No exfoliation of the graphite can be observed. In contrast, the heat-treated SLX50 graphite samples cooled under Ar atmosphere show an additional irreversible charge-consuming process manifested by an additional potential plateau during the first electrochemical lithium insertion (Fig. 2). The process starts at about 450 mV versus Li/Li<sup>+</sup> and was identified as the exfoliation of the graphite. The said potential plateau corresponds to the irreversible, charge consuming film formation process on the graphite surface freshly created by the exfoliation process. This relatively low potential plateau is typical for exfoliation in an EC based electrolyte [10]. The exfoliation phenomenon was also confirmed by SEM observations as shown in Fig. 3(b). As a consequence, this irreversible process of graphite exfoliation significantly increases the “loss” of the specific charge during the first electrochemical lithium insertion, as shown in Table 1.

The comparison of the electrochemical data with the graphite surface characteristics reveals that the electrochemical behavior of the graphite can be correlated to the structural modifications occurring during the treatments, as it will be discussed below.

The evolution of the ASA of the graphite leads to modifications of the galvanostatic curves and the irreversible charge loss. After heat treatment in argon, the decrease of the ASA induces an important increase in the irreversible “charge loss” which is characteristic for an exfoliation process, as confirmed by SEM observations (Fig. 3(b) being one example from many). It is interesting to note that, when the graphite sample heat-treated in argon is again exposed to air to increase the ASA (and consequently to increase the amount of surface defects), the exfoliation phenomenon is not observed anymore. This may be related to the surface reactivity against the electrolyte. In fact, the higher the amount of active surface sites at the graphite surface, the higher the graphite surface reactivity that can be expected. A graphite material with a low ASA value will thus show a low reactivity towards the electrolyte. As a result, the kinetics of the passivation layer formation will be slow and the passivation process will be not completed before the electrochemical exfoliation starts. The influence of the heat treatment time is in agreement with the above explanations; the longer the heat treatment time, the lower becomes the ASA and, consequently, the higher the irreversible “charge loss”.

We also observed that the potential at which the additional plateau appears becomes more positive when the ASA value decreases. In accord with the values of the irreversible specific charge, this can be explained by the fact that lower ASA values result in a lower overpotential for the exfoliation process of the graphite. This conclusion is obvious because the exfoliation creates new surfaces in contact with the electrolyte and, thus, the local current density decreases.

In contrast, the graphite material with a lower structural ordering (high ASA value) shows a higher reactivity towards the electrolyte and, thus, the kinetics of the formation of the passivation layer (SEI) will be enhanced. In this condition, the formation of the SEI layer is completed prior to the onset of the exfoliation. This is in agreement with the fact that the kinetics of formation of the passivation layer is related to the ASA.

#### 4. Conclusion

The stability toward exfoliation of highly crystalline graphite materials depends on their reactivity which is related to the surface properties of the graphite. We show here that the surface properties and especially the active sites of the highly crystalline graphite material have a significant influence on the electrolyte decomposition and passivation process during the first electrochemical lithium insertion and, thus, on the SEI layer formation.

The elimination of surface defects by heat treatment (decrease of the ASA) hinders the formation of the SEI and consequently favors the exfoliation of graphite. On the contrary, the increase in the ASA results in faster electrolyte decomposition and subsequent graphite surface passivation at potentials which are more positive than the potential at which the electrochemical exfoliation of graphite can be observed. It clearly appears that the passivation is kinetically enhanced at graphite surfaces with high ASA.

The electrochemical performance of graphite can be strongly modified by changing the ASA of the graphite. Whereas the graphite heat-treated in argon exfoliates during the first electrochemical insertion, its surface oxidation (causing a significant increase in the ASA) suppresses the exfoliation.

In short, we confirmed that the concept of active sites is a suitable tool to predict the passivation behavior of the graphite.

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