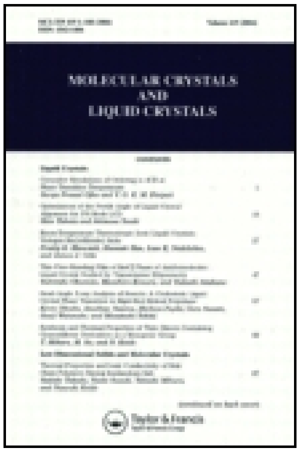

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Influence of Graphite Surface Modifications on Lithium Intercalation Properties

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The first galvanostatic reduction curve of the lithium intercalation into several treated graphite samples is discussed with respect to the effect of surface treatment on the intercalation process.

Keywords: graphite, intercalation, surface modification, lithium batteries

INTRODUCTION

Within the past few years carbon electrodes have achieved enormous technical importance for rechargeable lithium ion cells [1]. Fundamental to their successful operation is the formation of a protective film at the carbon surface resulting from the reductive decomposition of the electrolyte. Lithium ions are consumed for the formation of this protective film. This decreases the charge and energy density of the battery. In order to improve the charge density of a future lithium ion cell the irreversible lithium loss or, generally speaking, the charge loss in the first cycle should be minimised.

In our simple model, we distinguish between three types of charge losses (Fig. 1): (i) charge loss related to the reduction of the surface groups between ca. 3 V and ca. 0.8 V vs. Li/Li$^+$, (ii) the charge loss due to the film formation between ca. 0.8 V and ca. 0.2 V vs. Li/Li$^+$, and (iii) charge loss during the reversible insertion and extraction of lithium ions. A detailed discussion is published elsewhere [2].

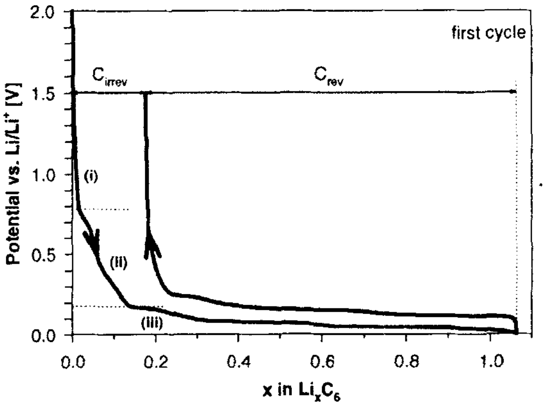

FIGURE 1 Lithium intercalation into graphite in the first cycle can be divided into three stages: (i) reduction of the surface groups, (ii) film formation, (iii) charge loss during the reversible insertion and extraction of lithium ions (electrolyte solution: 1*M* $LiN(SO_2CF_3)_2$ / DMC+EC).

We have studied the influence of the graphite surface modification on the lithium intercalation properties of the graphite TIMREX SFG 6, which has a high specific BET surface area of about 15 m^2/g and therefore a high charge loss [2]. If the surface groups of graphite are modified, e.g., by oxidation, reduction, or vacuum treatment, a different surface film is formed, which can be reflected in the shape change of the first galvanostatic reduction curve between 3 V and 0.2 V vs. Li/Li$^+$, regions (i+ii) in Fig. 1. The lithium intercalation properties of modified graphites are discussed with respect to minimising the charge loss in the first cycle.

EXPERIMENTAL

About 500 μm thick porous electrodes of 1.3 cm^2 geometrical area containing *ca.* 40 mg of graphite were prepared from graphite SFG 6 (TIMCAL G+T AG, formerly LONZA G+T AG) and 1.5 wt.% poly(tetrafluoroethylene) (PTFE) binder. The blend of graphite and binder was dried, then dry-mixed with 50 wt.% of NH_4HCO_3, pressed at ca. 3 t/cm^2, and finally vacuum-dried at 300 °C for 24 h. Porous electrodes resulted from the complete decomposition of NH_4HCO_3. More experimental details are described elsewhere [3].

The electrochemical studies were performed in hermetically sealed two electrode cells with a lithium counter electrode [4]. The cell components were arranged as in button cells. The working and counter electrodes were permanently sandwiched together under a pressure of ~2 kg/cm^2. The electrodes were separated by a glass fiber separator soaked with the electrolyte, 1*M* $LiN(SO_2CF_3)_2$ in EC/DMC (1:2 by weight; EC = ethylene carbonate, DMC = dimethylcarbonate). The graphite electrodes were galvanostatically cycled three times between 1.5 and 0.005 V vs. Li/Li^+. Our investigations focused mainly on the first cycle which was performed at a slow rate of ±0.01 mA/mg of graphite. The subsequent cycles were performed at a faster rate of ±0.05 mA/mg to test the stability of the electrode over several cycles.

RESULTS AND DISCUSSION

Graphite surfaces are typically covered with a variety of surface-functional groups like hydrogen, phenol, carbonyl, carboxyl, etc. Reducing the graphite surface groups by hydrogen gas at 900°C decreased the reversible specific capacity of the graphite by 10-20% from about 330 Ah/kg to the range between 260 and 290 Ah/kg. Thus, it is likely that the presence of hydrogen-containing surface groups is detrimental for the reversible lithium intercalation reaction as also described by Takamura and coworkers [5]. In order to confirm this hypothesis, we tried to eliminate the surface groups containing hydrogen by oxidising the carbon surface in air at three different temperatures. The optimum temperature for our surface oxidation process is approximately 600°C (Fig. 2). The corresponding sample consumes less charge in the regions (i+ii) than the original graphite sample (standard) or the graphite treated at 500°C or 700°C. Note that the galvanostatic reduction curve in region (i+ii) is also shifted to more negative potentials.

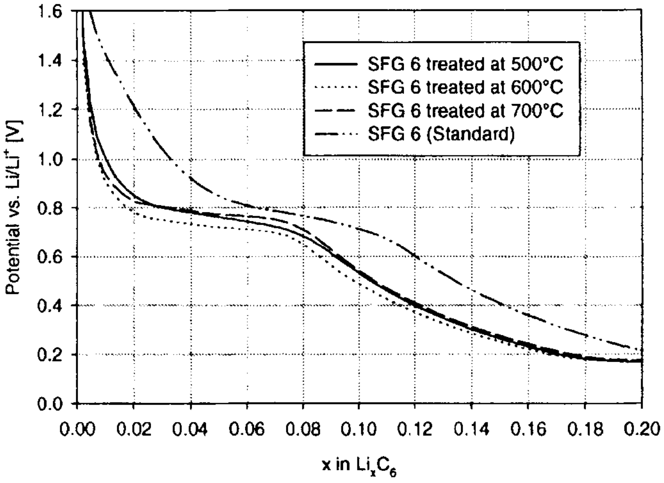

FIGURE 2 Comparison of the first galvanostatic reduction curves of different SFG 6 samples oxidised at three different temperatures in air.

Also slightly lower charge is consumed for the film formation when the graphite is treated in dynamic vacuum for 4 h at 900°C (Fig. 3). This may well be due to removal of detrimental surface groups like C-H groups.

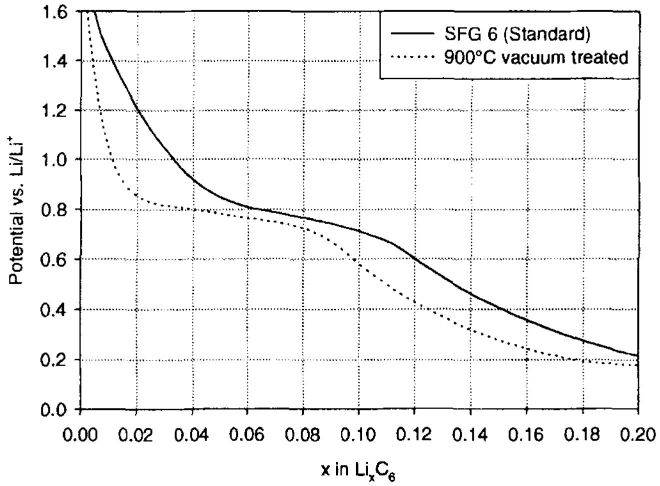

FIGURE 3 Effect of vacuum treatment on the first galvanostatic reduction curve.

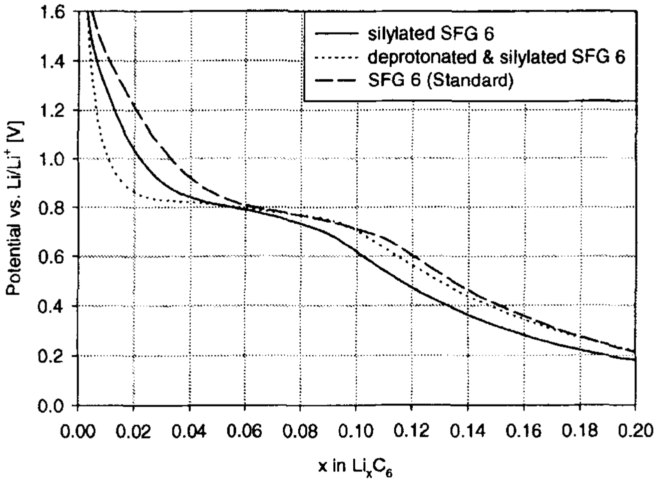

FIGURE 4 Effect of the silylation of SFG 6, with and without a pretreatment with butyllithium before the silylation.

In another approach we blocked the nucleophilic surface groups with trimethylsilyl groups. We treated the graphite with a solution of trimethylsilyl trifluoromethanesulfonate (Aldrich) in hexane. As a result, the charge loss between 3 V and 0.8 V vs. Li/Li$^+$ is reduced significantly as can be seen from

Fig. 4. For a more complete blocking of the groups, the graphite can be treated with ca. 1.6 *M* solution of butyllithium in hexane (Fluka), before it is silylated. Fig. 4 shows that the latter treatment further reduced the charge loss in region (i).

CONCLUSION

The nature of the graphite surface groups influences the charge loss and the first galvanostatic reduction curve in the first cycle, especially in the potential region ≥ 0.8 V vs. Li/Li$^+$. The best results have been achieved with oxidation, vacuum treatment, and silylation of the graphite.

Acknowledgement

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