Modifications of synthetic graphite for secondary lithium-ion battery applications

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Abstract

Experimentally, three types of synthetic graphite from TimRex (SFG44, SFG15 and KS6) were plated with copper electrolessly. The specific capacities of untreated TimRex samples are typically in the range of 140–280 mA h/g, with low coulombic efficiencies in the first few cycles of charge and discharge. Electroless copper plating on these graphites could substantially improve the material performance in discharge capacity and coulombic efficiency. Some improvement in high rate dischargeability was also observed. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the past decade, there has been a growing interest in the search for suitable carbon materials as an intercalation host (anode) for lithium-ion rechargeable batteries [1–4]. When graphite is used as an active material for the anode, lithium can be intercalated between layers of carbon in one lithium atom per six carbon atoms at maximum, in other words at most LiC_6. At the upper limit, theoretical capacity only by a reaction between carbon and lithium is 372 mA h/g (unit weight of carbon). A major problem in using graphite as the anode is a large irreversible loss between the first discharge and the first charge [5,6], and the inadequate high rate characteristics of the graphite. This irreversible loss is mainly believed to be due to electrolyte decomposition that results in the formation of a passivating film or solid electrolyte interphase (SEI) on the carbon surface [7]. Some Li are also consumed in the SEI formation process. This has important consequences for Li-ion cells. Since the only source of Li ions in conventional Li-ion cells is the lithium transition metal oxide cathode, any consumption of Li due to SEI formation leads to a capacity loss. Therefore, the amount of irreversible

capacity which occurs on the carbon during the first intercalation reaction of lithium must be minimized in practical cells.

Numerous studies of the chemical composition and the formation of SEI have been performed [8,9]. Peled et al. [10] showed that mild oxidation (burning) produces well-defined voids on the surface of the graphite. The voids, or nanochannels, are small enough to prevent cointercalation of the solvent molecule but allow Li-ion penetration. Ein-Eli and Koch [11] showed that chemical oxidation of graphite powder by strong oxidative agents increased the reversible capacity obtained during cycling from 370 to 430 mA h/g, whereas the irreversible capacity accompanying the first intercalation cycle was reduced.

Through a survey of various solvents and Li-based salt compositions, new electrolyte compositions leading to only 7% of irreversible losses in some types of graphite could be found [9]. However, with the same electrolyte, some other graphitic forms of carbons show losses as high as 25%. It is well known that most carbon materials differ in their morphology, specific surface area, defect density and so on. It can therefore be concluded that the surface states of carbon plays an important role in SEI formation.

The original goal of the present work was to investigate the possibility of using synthetic graphite (Timrex SFG44, SFG15 and KS6) as the negative electrode in lithium-ion rechargeable batteries. During the course of our study, we found that the material performance in key areas such as

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the amount of irreversible capacity, charge–discharge capacity and high rate capability are largely determined by the surface conditions of carbon. As an alternative to the previously stated methods of surface modification, electroless copper plating was used to alter the electrochemical properties of graphite in Li-ion intercalation and deintercalation reactions.

2. Experimental

Three types of synthetic graphite (Timrex SFG44, SFG15 and KS6) were used as the active materials in the negative electrodes of lithium-ion batteries. Synthetic graphite powders were added to a commercial electroless Cu plating formulation at 25°C for 5–30 min, which were then filtered and dried in vacuum. The working electrodes were prepared by blending the graphite powder with 10 wt.% of poly(vinylidene fluoride) (PVDF) binder, coating the anode mix on copper foils, drying the coated foils at 120°C for 24 h. Electrodes with typical loading of 7 mg/cm^2 were compressed at 3 T/cm^2. A lithium chip and a lithium foil were used as the reference electrode and the counter electrode, respectively. The electrolyte solution was 1 M LiPF$_6$ dissolved in a 1:1 (by volume) mixture of EC–DMC. Electrochemical measurements were carried out in a three-electrode cell. Two electrode cells with Li foils as the counter electrodes were used for charge/discharge cycling. The charge/discharge curves were measured in

the potential range of 0 to 2 V vs. Li/Li$^+$ at a current density of 0.4 mA/cm^2. The coulombic efficiency of a cycle (E_f) was defined as $E_f = (C_{disch}/C_{ch})100\%$, where C_{disch} and C_{ch} are the electrochemical charge passed during the discharge and charge operation of that cycle, respectively.

X-ray diffraction (XRD) measurements using a Philips diffractometer PW1710 and CuKα radiation (1.5418 Å) were used to determine the structures of synthetic graphite before and after surface modification.

3. Results and discussion

The typical values of reversible specific capacity (C_{disch}) and coulombic efficiency (E_f) of the graphite samples are given in Table 1. The reversible specific capacity is a measure of the extent of Li$^+$ deintercalation and the coulombic efficiency is the ratio between the charge consumed and charge released in a charge/discharge cycle. C_{disch} is about 140 mA h/g in the first cycle for untreated graphite and 280 mA h/g for treated graphite Coulombic efficiency is noticeably low in the first cycle for untreated graphite, but increases with increasing cycle number. The effect of cycling on coulombic efficiency for treated and untreated KS6 can be seen from Fig. 1. For untreated KS6, 10 cycles were needed before a nearly steady value of ~95% could be reached. For treated KS6, only four cycles were required. The BET surface areas of SFG44,

Table 1
Charge and discharge behaviour of synthetic graphites at 0.4 mA/cm^2 (57.1 mA/g)

|	SFG44 (mA h/g)		SFG15 (mAh/g)		KS6 (mA h/g)	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
First cycle C_{ch} (mA h/g)	354	359	363	358	370	394
First cycle C_{disch} (mA h/g)	235	283	211	269	141	284
First cycle E_f (%)	66.4	78.8	58.1	75.1	38.1	72
Second cycle C_{ch} (mA h/g)	348	331	359	347	193	312
Second cycle C_{disch} (mA h/g)	252	311	228	319	137	279
Second cycle E_f (%)	72.4	94.0	63.5	91.9	71	89
Third cycle C_{ch} (mA h/g)	341	319	348	320	170	302
Third cycle C_{disch} (mA h/g)	267	308	266	303	131	278
Third cycle E_f (%)	78.3	96.6	76.4	94.7	77.1	92
Fourth cycle C_{ch} (mA h/g)	338	310	341	315	155	288
Fourth cycle C_{disch} (mA h/g)	276	305	275	306	127	273
Fourth cycle E_f (%)	81.7	98.4	80.6	97.1	81.9	95
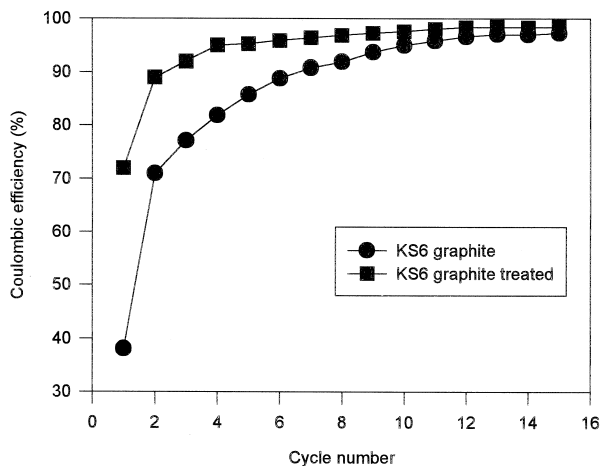
Fig. 1. Coulombic efficiency vs. cycle number for treated and untreated KS6 graphite anode at 0.4 mA/cm² (57.1 mA/g).

Table 2
Charge consumption in the various regions of the first charge curve

Type	C_{ch} (mA h/g)		
	I	II	III
SFG44 graphite untreated	50	68	236
SFG44 graphite treated	20	42	297

SFG15 and KS6 according to manufacturer's specifications are 4.3, 8.5 and 19.4 m²/g, respectively. From Table 1, the first cycle coulombic efficiency ranges from ∼ 38%, for the high surface area KS6, to ∼ 66%, for the low surface area SFG44. This observation is in line with the literature reports of the adversarial effect of large surface area on irreversible capacity loss [13].

Electroless copper plating on these graphite samples has resulted in increases in both the discharge capacity and the coulombic efficiency. As BET measurements did not indicate any significant changes in the surface areas due to electroless plating, the observed improvements in material performance was not based on a surface area effect.

A closer examination of the galvanostatic charging curve can lead to a better understanding of the events that occur during charging in the first cycle. The charging curve can be divided into three broad regions (I, II and III) based on the sudden changes in the cell voltages [7]. Fig. 2
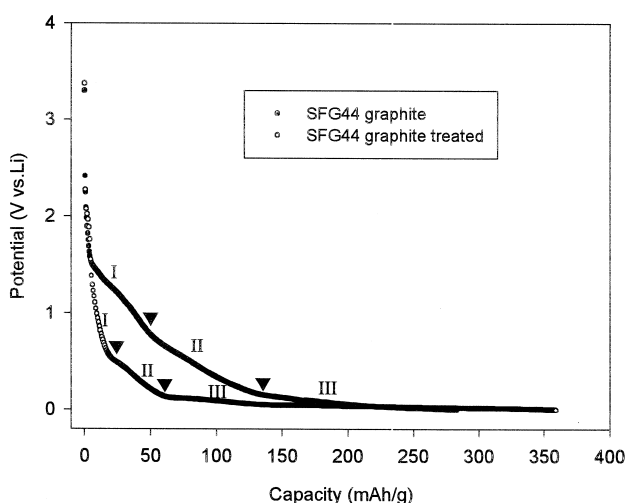

Fig. 2. First charge/discharge curves of untreated and treated SFG44 graphite anodes showing the subdivision of the curves into three potential regions, I, II and III.

shows the first charging curves of the untreated and treated graphite SFG44 as an example. The main reaction in Region I is the SEI formation/electrolyte decomposition on the external graphite surface [7,12]. (The external surface is what is measurable by the BET method.) In the potential range of ∼ 0.8 to ∼ 0.2 V vs. Li/Li⁺ (Region II), the major reaction is thought to be solvated lithium ion intercalation [7,12]. Solvent-free lithium ion intercalation may also proceed to some extent in this region [6]. The naked intercalated lithium ion may migrate to the graphite bulk and be reversibly deintercalated later, or it may react with the electrolyte if the electrode is insufficiently protected by the SEI. The main reaction in Region III (< 0.2 V) is the reversible formation of subsequent stages of the binary lithium/graphite intercalation compounds (Li_xC_6). The stages are represented by potential plateaus in this region. At the same time, a considerable charge loss may occur if the SEI is not fully formed, necessitating the continuation of the above stated reaction between intercalated lithium ions and the electrolyte to build up the SEI layers. The estimated amount of charge consumed in each region (C_{charge}) is given in Table 2. It is apparent from Fig. 2 and Table 2 that irreversible losses caused by reactions in Regions I and II were effectively suppressed after copper plating. There is virtually no irreversible loss in Region III for modified and unmodified graphite. Copper plating therefore appears to have reduced the irreversibility due to SEI formation. It is surmised that copper plating has constricted the channels through which solvated lithium ions intercalate into the graphite host. This has effectively clamped down on one undesirable mechanism for irreversible capacity loss. Work is in progress for a further understanding of this phenomena.

Fig. 3 shows the d(002) X-ray diffraction peaks of the untreated and treated graphite. There is no positional shift and the sharp peaks are indicative of a high degree of crystallinity. The interlayer (d_{002}) distance remains constant at 3.354 Å for the treated graphite. It can therefore be concluded that copper plating has not brought about any crystallographic changes to the graphite structure.

The cyclic voltammograms of copper plated SFG44 and SFG44 are shown in Fig. 4. The cathodic and anodic peaks in the potential range of 0–0.4 V corresponding to the intercalation and deintercalation of lithium ions into or from graphite are substantially higher after copper plating. The cathodic and anodic current peaks were also increased in varying degrees for the other two types of synthetic
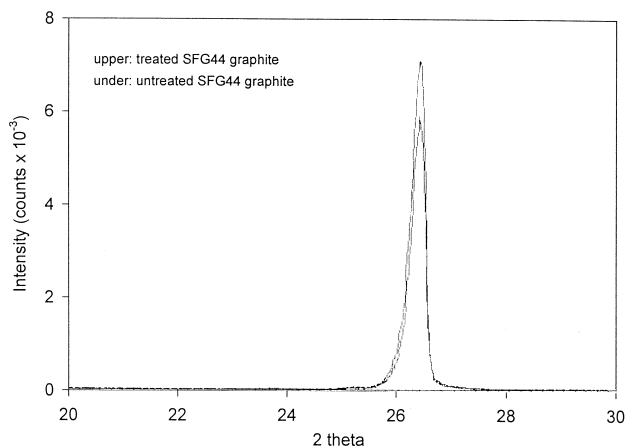
Fig. 3. XRD patterns of synthetic graphite.

Fig. 5. High rate capabilities of untreated and treated SFG44 graphite electrodes.

graphite. The electrochemical characteristics of carbon is closely related to the carbon surface properties which can be moderated through a surface treatment such as that described here. Usually surface species such as –OH, $=O$ and H_2O are performance inhibiting as they tend to extent of lithium intercalation and deintercalation reactions, for example, by hindering the transfer of lithium ions from the surface to the bulk. Copper plating may lead to a reduction in the amount of these surface inhibiting species, either through embedding or some other more complex mechanisms.

High rate dischargeability is one of the desirable attributes of a practical cell. High rate dischargeability was slightly improved for graphite by electroless copper plating (Fig. 5). At the current density of 14.3 mA/g (0.1 mA/cm^2), the capacity of untreated SFG44 in the fourth cycle was 81% of the theoretical capacity at 303 mA h/g. The capacity was reduced to 64% of the theoretical value (240 mA h/g) when the current density was increased to 85.7 mA/g (0.6 mA/cm^2). After SFG44 was modified by
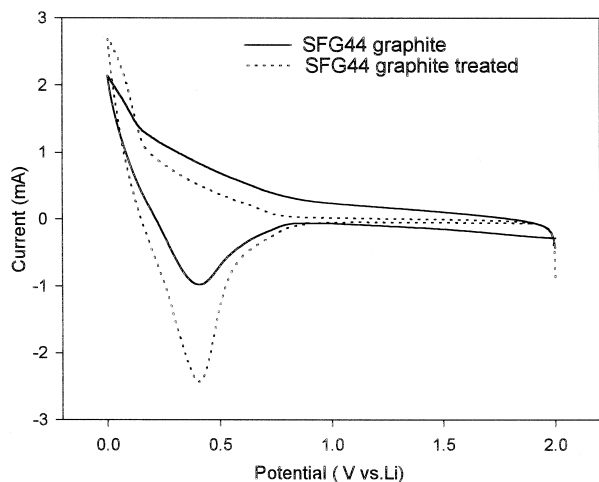
electroless copper plating, the capacity in the fourth cycle at 85.7 mA/g was increased to 77% of the theoretical value (285 mA h/g). The increase in high rate dischargeability due to copper plating is rather prominent.

4. Conclusions

Lithium ion intercalation into three types of synthetic graphite (SFG44, SFG15 and KS6) have been examined. The discharge capacities for the untreated graphite range from ∼ 140 mA h/g for KS6 to ∼ 280 mA h/g for SFG44 and SFG15, and the coulombic efficiencies in the first few charge and discharge cycles have typically low values Electroless copper plating on these graphite samples were found to substantially increase their discharge capacities and coulombic efficiencies. The cathodic and anodic current peaks in the potential range 0–0.4 V of the cyclic voltammograms were also correspondingly increased. High rate dischargeability was slightly improved after electroless copper plating. BET measurements did not indicate significant changes in the specific surface after copper plating. The improvement in electrochemical performance due to the reduction in irreversible charge losses is therefore not a surface area effect.

Fig. 4. Cyclic voltammograms of untreated and treated SFG44 graphite at 1 mV/s.

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