ELSEVIER

Journal of Power Sources 97–98 (2001) 126–128

JOURNAL OF POWER SOURCES

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Surface modification of graphite anodes by combination of high temperature gas treatment and silylation in nonaqueous solution

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Received 6 June 2000; accepted 11 December 2000

Abstract

Graphite surface modification by silylation in nonaqueous solution has been examined. Silane coupling with hydroxyl-containing carbon surface species, such as hydroxyl-groups and adsorbed water is assumed to be the main surface reaction introduced by this modification treatment. In terms of reduced irreversible charge losses, best results were obtained when graphites pre-oxidized in oxygen atmosphere at elevated temperatures have been silylated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium-ion battery; Graphite anode; Surface modification; Silane coupling; Solid electrolyte interphase

1. Introduction

Appropriate surface modification of graphitic carbons is a useful measure to improve the carbon anode performance in lithium-ion batteries. In particular, the irreversible charge losses associated with the formation of the solid electrolyte interphase (SEI) [1] on carbon anodes, may be considerably reduced after effective treatment. The work of Takamura's group [2–8] and Peled and coworkers ([1]) is mentioned here representative for the substantial work, which has been done in this field.

Recently, [9–13], we developed a two-step gas treatment procedure, which allows to modify carbon surface parameters, such as chemical composition (surface groups (–COH, –COOH, etc.)) and surface morphology, quite selectively. The process involves a "pre-cleaning" step in inert Ar atmosphere at elevated temperatures, in which the original surface groups are (partially) removed. This creates highly reactive carbon surface sites ("dangling bonds"). Then, the "cleaned" carbon surfaces are exposed to (reactive) gaseous partners, e.g. O_2 or others at a certain temperature and for a certain time (see [9–14] and Fig. 1).

Silylation of the carbon surface was suggested by Murray and coworkers in the mid 1970s [15,16]. In order to block surface species like hydroxyl-groups and water, which were considered to increase the irreversible capacity losses during charge of the carbon anode, Takamura et al. [2] and Joho et al [17] have applied such a silane coupling and observed small reductions of the irreversible charge losses during the first charge.

Oxidative or reductive pre-treatments of the carbon surface in order to facilitate the reaction with various coupling reagents, which can be covalently bonded to specific carbon surface groups created by the treatment, for example, the oxidative pre-treatment of carbon fibers used for the preparation of carbon fiber reinforced polymers [18], are well known in carbon (electro-) chemistry. Here, we report on the anode performance of graphites, which have been pre-treated by a long-term oxidation at elevated temperature in oxygen atmosphere according to the procedure shown in Fig. 1, and then have been subjected to further chemical surface modification by silane coupling in nonaqueous solution.

2. Experimental

Synthetic graphite TIMREX® SFG 44 (Timcal group) was heated under Ar flow in a quartz glass tube placed in a tube furnace by increasing the temperature from room temperature up to 1000°C with a 20°C min^{-1} ramp. Afterwards, the samples were kept under Ar flow at 1000°C for 1 h. Then, the samples were heat-treated under O_2 at $T_2 = 420°\mathrm{C}$

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PII: S0378-7753(01)00524-9

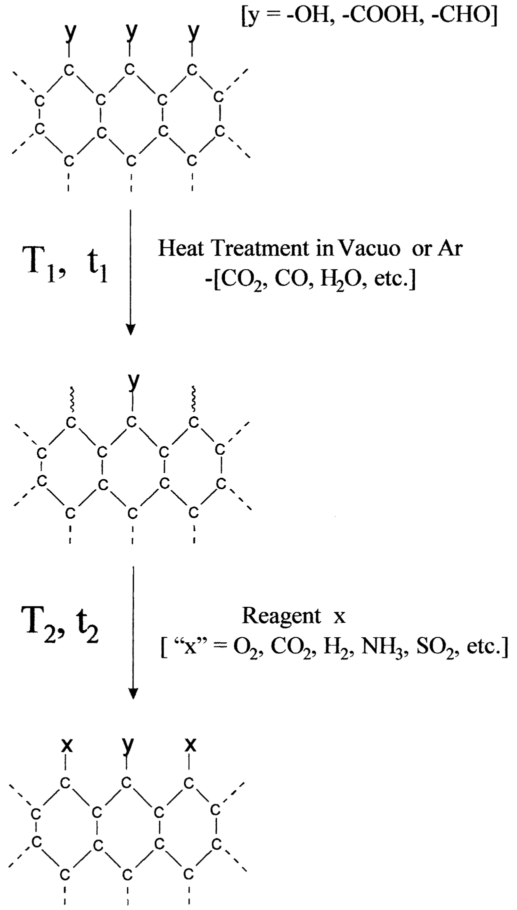

Fig. 1. Two-step pre-treatment of carbon surfaces via reaction of "dangling bonds" (details, see text).

for $t_2 = 60$ h. After treatment, the glass tube was cooled down to room temperature under Ar flow again.

For silylation, we adapted the procedure reported in [19]. The silane coupling of the graphites was done by treating approximately 0.5 g of graphite (pre-treated or untreated) in a 10/1 (by volume) mixture of hexamethyldisilazane (HMDS) and trimethyl chlorosilane (TMCS). The HMDS reacts with hydroxyl-containing surface groups of the graphite material (hereafter abbreviated to ROH) whereby ammonia is eliminated (Eq. (1)). The addition of the effective silyl donor TMCS increases the degree of silylation (Eq. (2)). Hence, apart from the silylated surface group ($ROSiMe_3$) the complete reaction (Eq. (3)) yields NH_4Cl as further product. The NH_4Cl is removed by washing the graphite with THF.

$$2ROH + Me_3SiNHSiMe_3 \rightarrow 2ROSiMe_3 + NH_3 \qquad (1)$$

$$ROH + Me_3SiCl \rightarrow ROSiMe_3 + HCl \qquad (2)$$

$$3ROH + Me_3SiNHSiMe_3 + Me_3SiCl \rightarrow 3ROSiMe_3 + NH_4Cl \qquad (3)$$

Electrodes were made from the dried samples and 4 w/o poly(vinylidene) fluoride binder. As electrolyte we used 1 M $LiClO_4$ dissolved in a 1/1 (by volume) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). All electrolyte components were supplied by Merck and had battery grade purity.

3. Results and discussion

Whereas the silylation of the pristine (untreated) graphite (Table 1a and b) causes no significant change in the discharge capacities and the discharge/charge efficiencies, silylation after 60 h pre-oxidation in oxygen considerably improves the efficiencies, i.e. reduces the irreversible charge losses, not only in the first but also in the later cycles (Table 1d). This is evidently not due to the pre-oxidation step, which yields even worse performance compared to the untreated graphite, both with respect to discharge capacities and with respect to efficiencies (Table 1a and c, see also [14]).

For effective silylation, the carbon needs an oxidative pre-treatment creating anchoring groups for the silanes on the surface. As oxidized prismatic surfaces of graphite are quite hydrophilic, one might expect that also the water content on the carbon surface is high and that the silanes react with the adsorbed water, creating further surface modification.

The improved anode performance can be expected to be due to the introduction of a silane-containing surface film prior to the first charge of the graphite. Several possible

Table 1
Charge/discharge performance of TIMREX® SFG 44 synthetic graphite[a]

Cycle number	$C_{discharge}$ (Ah kg^{-1})	C_{charge} (Ah kg^{-1})	Efficiency (%)
(a)			
1	339	406	83.1
2	339	359	94.2
3	340	356	95.4
4	340	350	97.6
(b)			
1	338	403	83.4
2	338	357	94.0
3	341	357	95.1
4	341	352	97.2
(c)			
1	323	397	80.1
2	320	352	91.0
3	320	346	94.0
4	318	340	94.6
(d)			
1	336	378	89.2
2	340	350	97.1
3	341	350	97.4
4	338	346	97.6

[a] (a) Untreated; (b) untreated and silylated; (c) after outgassing in Ar and subsequent treatment with O_2 at 420°C for 60 h; (d) after outgassing in Ar, treatment with O_2 at 420°C for 60 h and silylation. $i = \pm 20$ mA g^{-1}, cut-off = 0.024/2.00 V vs. Li/Li^+.

explanations for the improvement can be made: (i) the silane film has a predominantly organic character, i.e. can be penetrated by the organic electrolyte. A more favorable SEI formation underneath the "silane curtain" may thus take place; (ii) the silylation changes the surface chemistry, the surface area and/or morphology of the graphite; (iii) detrimental water impurities are consumed by reaction with silanes; (iv) the silylated surfaces may offer more favorable anchoring sites for the solid electrolyte interphase film; (v) finally, a change of the electrolyte wettability of the samples (silylated surfaces are highly lyophobic) should be regarded as well.

4. Conclusion and outlook

Silylation in nonaqueous solution is an effective measure for the reduction of irreversible capacities of graphite electrodes. Best results were obtained when pre-oxidized graphites were silylated. Apparently, the oxidative pretreatment and the silylation procedure have to be carefully coordinated with respect to each other for an optimum anode performance. Further investigations on the nature and the composition of the silylated surfaces are underway. Future work will be also focused on other coupling agents.

Acknowledgements

This work has been supported by the Austrian Science Fund in the "Electroactive Materials" special research program and by Mitsubishi Chemical Corporation. We thank the Timcal group (Bodio, Switzerland) and Merck (Darmstadt, Germany) for the donation of samples used in this study.

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