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Modified carbons for improved anodes in lithium ion cells

H. Buqa[a], P. Golob[b], M. Winter[a,*], J.O. Besenhard[a]

[a]*Institute for Chemical Technology of Inorganic Materials, Graz University of Technology, Stremayrgasse 16, A-8010 Graz, Austria*
[b]*Research Institute for Electron Microscopy, Graz University of Technology, Steyrergasse 17, A-8010 Graz, Austria*

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Abstract

A novel, quite flexible strategy for the surface pre-treatment of graphite anodes for lithium ion cells has been developed. The treatment involves a high temperature cleaning step in inert Ar atmosphere before treatment with gaseous reactants such as CO_2 or O_2. The effects of surface modification on the formation of the solid electrolyte interphase (SEI) and the corresponding irreversible charge losses are discussed by way of several examples. Morphology changes due to burn-off of carbon are particularly highlighted.

Keywords: Lithium ion battery; Graphite anode; Carbon surface; Carbon surface modification; Solid electrolyte interphase

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1. Introduction

The irreversible lithium, electrolyte and charge losses (C_{irr}) associated with the formation of the solid electrolyte interphase (SEI) on graphite anodes in lithium ion cells have to be minimized because they are detrimental to the specific energy of the cell [1–3]. Surface properties of the graphite anode material, such as surface area [4], porosity, morphology and chemical composition [5] are known to have substantial effects on C_{irr}. For an optimum anode performance, a careful selection of the graphite material and/or an appropriate chemical surface modification prior to electrochemical operation, both considering the desired surface properties, is obviously advantageous.

In order to understand the influence of the graphite surface and of graphite surface modification on SEI formation and C_{irr}, it is helpful to relate the formation of the SEI on carbons to ‘‘electropainting’’ (or ‘‘electroplating’’), as an electronically insulating film has to be deposited by an electrochemical process such as a ‘‘solution–precipitation’’ process (‘‘SEI-plating’’ or ‘‘filmplating’’, Fig. 1).

Our concept for graphite surface pre-treatment primarily focuses at a change of the surface chemical composition, in particular at the prismatic surfaces of graphite. It involves two independent steps: Firstly, reactive carbon surface sites (‘‘dangling bonds’’) are created by ‘‘desorption’’ of the pristine surface groups in inert atmosphere (Ar) at a certain temperature T_1 for a certain time t_1. Then, the ‘‘cleaned’’ carbon surfaces are exposed to reactants, such as O_2, CO_2, NH_3, N_2, SO_2, H_2S, C_2H_2, etc. at a temperature T_2 ($T_2 \leq T_1$) for a certain time t_2. In addition to a modification of the surface chemical composition, reactive gases may cause a ‘‘burn-off’’ of carbon resulting in a change of the carbon surface morphology. The large number of variables such as the type of reactive partner(s), T_1, T_2, t_1, and t_2 allows to specifically adjust the pre-treatment procedure, and hence, to tailor the carbon surface to some extent [5–8].

Here, we show electrochemical and electron microscopy results of graphite anodes treated with O_2 and CO_2 at various temperatures. XPS data related to this article can be found elsewhere [8–10].

2. Experimental

2.1. Synthesis of O_2- and CO_2-modified graphites

Synthetic graphite TIMREX® SFG 44 (Timcal Group, Brunett–Emmer–Teller (BET) surface area: 4.1 $m^2\ g^{-1}$) 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 one hour. Then, the samples were heat-treated under O_2 or CO_2 flow at certain temperatures T_2 for different times t_2 (details are

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[*] Corresponding author. Tel.: +43-316-873-8268;
fax: +43-316-873-8272.
E-mail address: winter@ictas.tu-graz.ac.at (M. Winter).

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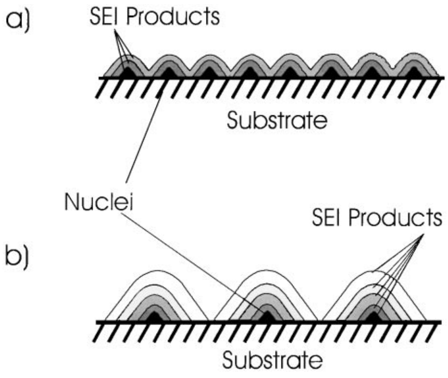

Fig. 1. Model: "plating" of SEI products on carbon. Composition and in particular, morphology of the SEI deposit are controlled by the "plating conditions", i.e. by the electrolyte composition, the pre-treatment of the carbon "substrate" surface towards a favorable morphology and chemical composition, the current density, etc. (a) Plating conditions, favoring a higher degree of nucleation, result in a more compact and dense SEI. (b) Plating conditions, which facilitate the crystal growth of the initially formed nuclei, induce the formation of a more rough SEI deposit, which requires more SEI products to get pin-hole-free, i.e. consumes more irreversible charge.

given below). After treatment, the glass tube was cooled down to room temperature under Ar flow again.

2.2. Electrolytes, electrodes and cells

Electrodes (above graphites and 4 wt.% poly(vinylidene) fluoride (Aldrich) as binder) and cell assembly were accomplished as described elsewhere [11]. Ethylene carbonate (EC), dimethyl carbonate (DMC), and $LiClO_4$ (all Merck, battery grade) were used as received. The ratio of solvents in the EC/DMC electrolyte mixture is given in volume percent.

2.3. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) investigations have been performed with a LEO DSM 982 Gemini scanning electron microscope (cathode: Schottky emitter). An electron energy of 5 keV has proved optimum for the graphite specimens under investigation. The graphite powder has been scattered across a double-sided electrically conductive adhesive carbon tape.

3. Results and discussion

3.1. Mild oxidation with carbon dioxide and oxygen

In comparison to oxygen, CO_2 is a very mild oxidant towards carbon. The oxidation power of CO_2 is described by the "Boudouard-equilibrium" [12], as denoted in Eq. (1)

$$172.58\,\mathrm{kJ} + CO_2 + C \rightleftharpoons 2CO \tag{1}$$

The above reaction is endothermal that, e.g. at 500°C carbon does basically not react with CO_2, whereas at 1000°C CO_2 is able to combust slowly the carbon. By contrast, even at temperatures below 500°C oxygen is able to combust carbon.

3.2. Morphology of the carbon surface

Burn-off of carbon by CO_2 takes place at $T_2 = 1000°C$ after $t_2 = 15$ min treatment. This results in a rough morphology of the prismatic carbon surfaces (Fig. 2d). Treatment at $T_2 = 500°C$ ($t_2 = 15$ min) shows no significant morphology changes (Fig. 2c), indicating no significant burn-off in comparison to the untreated graphite (Fig. 2a) and the graphite after Ar-cleaning, i.e. without further gas treatment (Fig. 2b). These observations are in line with the Boudouard equation. The mildness of the oxidation treatment with CO_2 is indicated by the fact, that even at 1000°C

Table 1
Specific charges for charge (C_c) and discharge (C_d) as well as discharge/charge efficiencies (efficiency: ratio of discharge capacity to charge capacity) of graphite TIMREX® SFG 44[a]

cycle number	C_d (Ah kg^{-1})	C_c (Ah kg^{-1})	Efficiency (%)
(a) Untreated			
1	339	406	83.1
2	339	359	94.2
3	340	356	95.4
4	340	350	97.6
(b) After "cleaning" in Ar at 1000°C			
1	336	404	83.4
2	336	357	94.5
3	338	354	95.5
4	340	351	97.4
(c) After Ar-cleaning and subsequent gas treatment with CO_2[b]			
1	401	336	83.8
2	354	336	94.9
3	348	333	95.7
4	344	336	97.7
(d) After Ar-cleaning and subsequent gas treatment with CO_2[c]			
1	344	401	88.3
2	349	368	96.6
3	352	362	97.3
4	349	357	98.1
(e) After Ar-cleaning and subsequent gas treatment with O_2[d]			
1	349	405	88.7
2	351	362	97.1
3	349	358	97.5
4	349	354	98.9
(f) After Ar-cleaning and subsequent gas treatment with O_2[e]			
1	323	397	80.1
2	320	352	91.0
3	320	346	94.0
4	318	340	94.6

[a] Electrolyte: 1 M $LiClO_4$ in EC/DMC (50/50). Constant current charge/discharge cycling with $i = \pm 20$ mA g^{-1}, cut-off: 2.0/0.024 V versus Li/Li^+.

[b] At $T_2 = 500°C$ for $t_2 = 15$ min.

[c] At $T_2 = 1000°C$ for $t_2 = 15$ min.

[d] At $T_2 = 420°C$ for $t_2 = 15$ min.

[e] At $T_2 = 420°C$ for $t_2 = 60$ h.

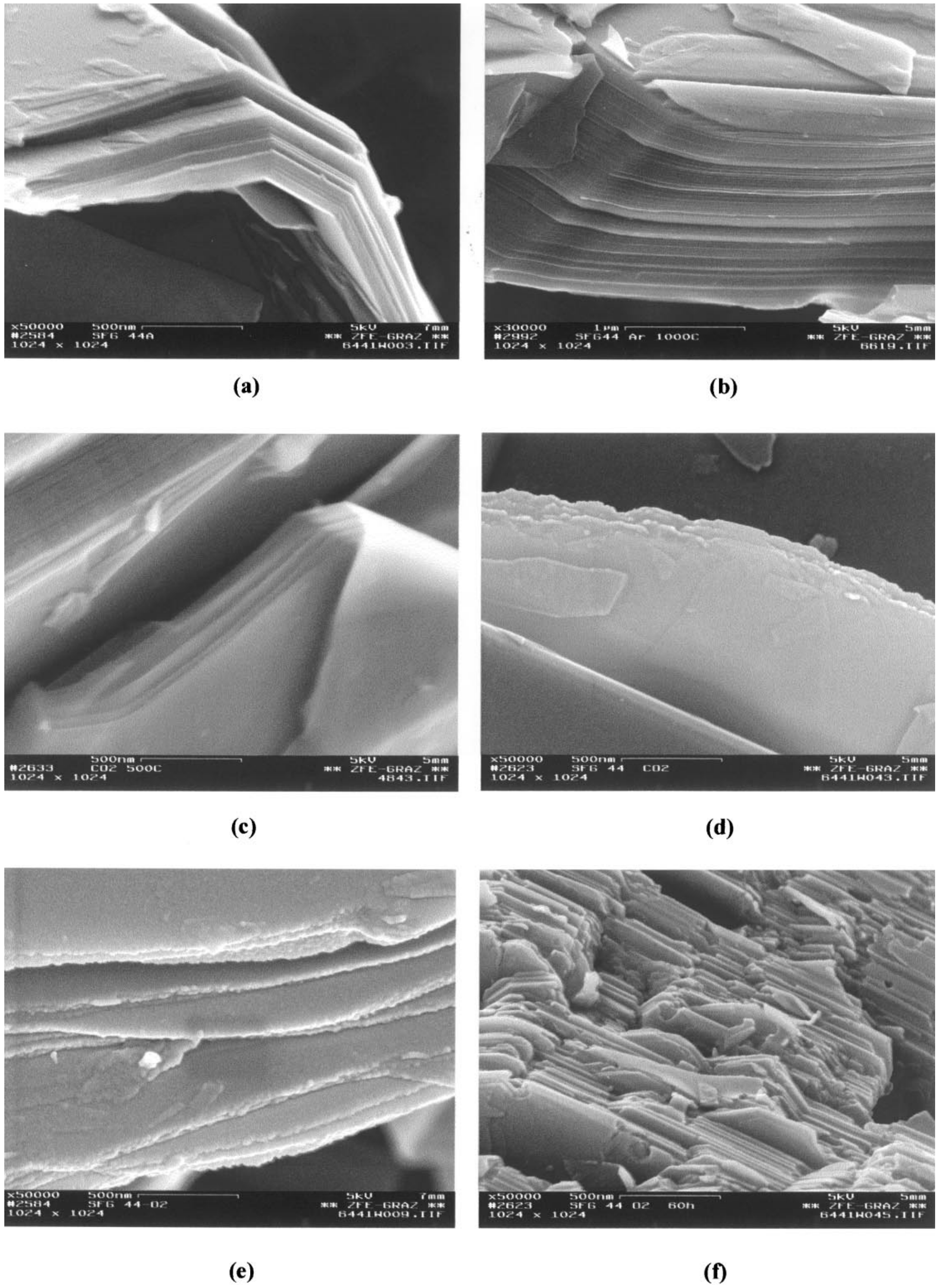

Fig. 2. SEM pictures of TIMREX® SFG 44 synthetic graphites: (a) untreated; (b) after "cleaning" in Ar at 1000°C; (c) after Ar-cleaning and subsequent gas treatment with CO_2 at $T_2 = 500°C$ for $t_2 = 15$ min; (d) after Ar-cleaning and subsequent gas treatment with CO_2 at $T_2 = 1000°C$ for $t_2 = 15$ min; (e) after Ar-cleaning and subsequent gas treatment with O_2 at $T_2 = 420°C$ for $t_2 = 15$ min; (f) after Ar-cleaning and subsequent gas treatment with O_2 at $T_2 = 420°C$ for $t_2 = 60$ h.

only the external prismatic (edge) surfaces of graphite are attacked.

Treatments with O_2 at $T_2 = 420°C$ for different times t_2 result in divers degrees of burn-off of graphite. The morphology changes at the prismatic surfaces range between "nano-roughness" (or "submicro-roughness", Fig. 2e) after 15 min treatment and the formation of "channel-like" prismatic surface morphologies after 60 h treatment (Fig. 2f). SEM pictures of graphites treated for times 15 min $< t_2 <$ 60 h show morphologies in between and are not shown here for space reasons.

3.3. Anode behavior

Table 1 gives the charge and discharge capacities as well as the corresponding efficiencies of the above graphite samples. Three categories of results can be classified: (i) treatments which showed apparently no morphology changes, i.e. ''Ar-cleaning'' (Table 1b) or CO_2-treatment at 500°C (Table 1c), had no significant influence on the anode behavior with comparison to the untreated graphite (Table 1a); (ii) 15 min treatment at 1000°C with CO_2 (Table 1d) and at 420°C with O_2 (Table 1e) bring about significant reductions of C_{irr} in the first and in the later cycles (expressed as an increase of the discharge/charge efficiencies) with comparison to the untreated sample (Table 1a). Apparently, a nano-rough morphology of the prismatic surfaces of the graphite favors SEI formation which is associated with low C_{irr}. One might conclude that this specific surface roughness offers favorable anchoring/nucleation sites for SEI plating. This beneficial behavior is apparently not counteracted by an increase of surface area due to burn-off, as BET surface area measurements and the determination of the weight loss of carbon after treatment reveal no significant surface area and weight changes (both $< 1\%$). (iii) Longer treatments with O_2, e.g. for 60 h decrease both the discharge capacities and the efficiencies. This may be related with unfavorable morphology changes or an increase of the BET surface area by about 20% after long treatment.[1]

4. Conclusion

A systematic method for surface modification of graphites has been presented. Morphology changes due to mild treatment with CO_2 or O_2 have been related with the electrochemical performance. Improved performances have been found for graphites with ''nano-rough'' prismatic surface morphologies.

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[1] Changes of the chemical composition are not discussed here. For further information, see [8–10].