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Siloxane-Impregnated Graphite Anode for Li-Ion Cells With PC-Based Electrolytes

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It has been demonstrated that pre-treatment (impregnation) of graphite anodes in a polyether functionalized disiloxane agent prevents graphite flake exfoliation and electrode degradation in Li-ion cells with electrolytes based on propylene carbonate (PC) as single electrolyte solvent. This beneficial effect has been evidenced to strongly depend on the concentration of the impregnation bath. For 100% concentration (pure siloxane), SEM images do not exhibit visible signs of flake splitting and the corresponding galvanostatic charge/discharge curves exhibit conventional lithium intercalation behavior, with reversible capacity approaching 300 mAh g^{-1}. *Post-mortem* EDX analysis of cycled electrodes revealed the presence of silicon species in the passive layers on graphite. The proposed approach can be regarded as alternative for conventional exfoliation-suppressing methods relying on bulk electrolyte additives.

Keywords: lithium intercalation, Li-ion battery, graphite exfoliation, disiloxanes, silicon podands

1. INTRODUCTION

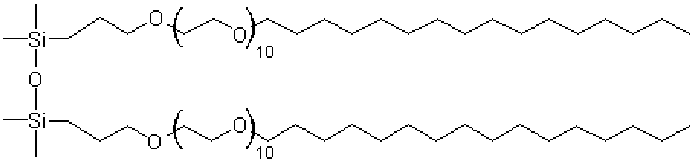
In recent years a very considerable number of works have been devoted to the problem of suppression of detrimental graphite anode exfoliation in Li-ion batteries with electrolytes based on propylene carbonate. These works have been mostly motivated by the need of searching for electrolyte solvents alternative to commonly applied ethylene carbonate (EC). EC has proved to be extremely effective in terms of promoting the formation of high quality, thin and compact passive layer on graphite anode (also called solid electrolyte interphase – SEI). However, EC is also known to have limited applicability in batteries designed for low temperature applications, which is due to its relatively high melting point (34-37 ˚C). PC is potentially an ideal replacement for EC owing to such properties as high dielectric constant $\varepsilon = 64$ and high polarity. Unfortunately, PC is also inherently incompatible with most graphitic anodes, which is caused by the fact that it tends to co-intercalate together with lithium cation into the graphite crystal lattice. During the first charging of the electrochemical cell PC molecules are being electro-reduced between the graphene sheets with the evolution of gaseous products, leading to the multiple splitting and degradation of graphite flakes. The most effective strategies to overcome this difficulty include: a) application of bulk functional electrolyte additives (vinylene carbonate [1-4], methyl acetate [5], isocyanates [6-8], silanes and siloxanes [9-14] and b) protecting the graphite flakes by a suitable "solid" micro-coatings (carbon, Ag [15], Cu [16], Cu_2O [17], TiO_2 [18] and MoO_3 [19].

This paper reports a novel approach to the problem of avoiding graphite anode degradation in propylene carbonate. The proposed method relies on pre-treatment (impregnation) of graphite electrodes in a suitable film-forming agent. 1,1,3,3-tetramethyl-1,3-bis(3-(ω-hexadecyloxy-deca(ethylenoxy)propyl)disiloxane has been identified as an effective protective agent. According to a number of reports, liquid acyclic silanes and siloxanes with polyoxaethylene functional groups appear to have significant potential for the application as electrolyte solvents/co-solvents and functional electrolyte additives in Li-ion batteries [20-24]. Ether oxygen atoms contribute to dissociation of lithium salts, hence these species can be added to the electrolyte in relatively large quantities without deterioration of conductivity. Specific molecular features, such as the number and length of the polyether segments, as well as the presence of additional functional groups, are known to impact greatly their behavior towards alkali metal cations. Phenomena like self-assembling and complex stabilities are being increasingly investigated by the sub-domain of supramolecular chemistry devoted to so-called silicon podands.

In this paper it is demonstrated that graphite electrodes modified in the proposed way can successfully operate in Li-ion anodic half-cells with electrolyte based on PC as sole solvent, without any bulk additives.

2. EXPERIMANTAL SECTION

1,1,3,3-tetramethyl-1,3-bis(3-(ω-hexadecyloxy-deca(ethylenoxy)propyl)disiloxane (designated hereafter as "siloxane") has been synthesized according to the procedure described in [13].



Graphite electrodes were prepared in a conventional way by doctor-blading a graphite containing slurry onto a copper foil current collectors, followed by vacuum drying at 120 ˚C. The electrodes were not roll-pressed. The electrodes were prepared in the form of round pellets, 10 mm in diameter. Impregnation of the electrodes was accomplished in a simple procedure by immersing them in siloxane-based baths for 24 h. After taking out from the baths, the electrodes were pressed lightly between two pieces of blotting paper in order to remove the excess of impregnating agent. All the operations were carried out in argon-filled glove box (humidity level less than 2 ppm). After evaporating (if necessary) the acetonitrile, the electrodes were put into standard two-electrode electrochemical cells with lithium counter electrodes, Celgard separators and the electrolyte being a 1M solution of $LiPF_6$ in PC ($LiPF_6$ - Aldrich, 99.99 %; PC - Merck, 99.7 %, anhydrous). The anodic half-cells were subjected to constant current charging/discharging at the current density of 10 mA per gram of graphite active mass, between 0 and 2 V vs. Li/Li^+.

Post-mortem SEM/EDX analysis of cycled electrodes was carried out using Vega 5135MM apparatus (Tescan). After removing from the cells and before SEM/EDX investigations the electrodes were carefully washed with propylene carbonate and dried under vacuum at 120 °C for 24 h, so as to remove all the remaining liquid electrolyte species.

3. RESULTS AND DISCUSSION

Graphite flakes after the electrode impregnation are covered with a thin layer of physisorbed siloxane. This is evidenced by the reflection spectrum recorded for the electrode surface (solid line in the Fig. 1) after impregnation in the 100% siloxane bath. For comparison, FTIR spectrum of the siloxane itself, obtained in a conventional way, has been showed (dotted line). Thus it is demonstrated that surface modified graphite anode has been manufactured by the described technique.

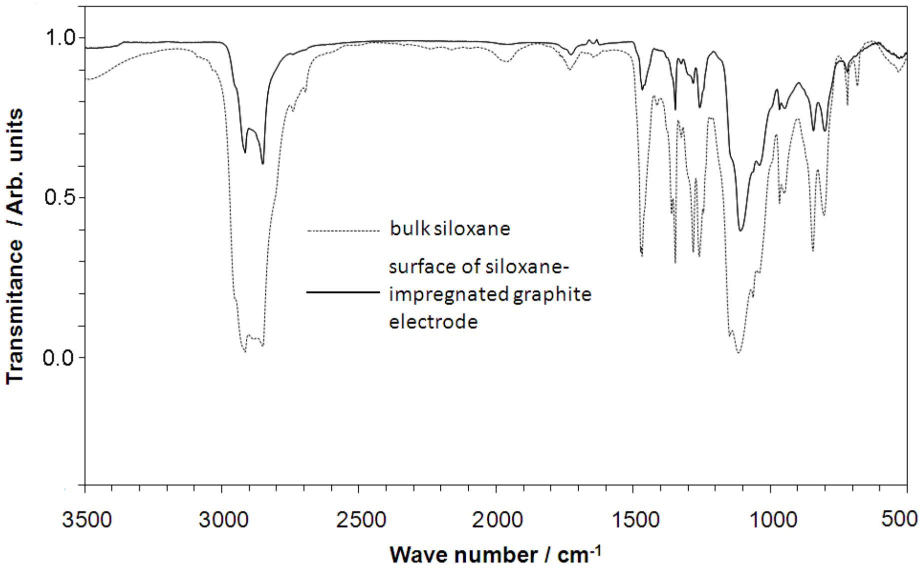


Figure 1. FTIR spectrum of the surface modified graphite electrode; as the reference – spectrum of the impregnation agent

Fig. 2 presents first cycle charge/discharge galvanostatic curves recorded for the anodic half-cells with graphite electrodes impregnated in baths with three concentrations of siloxane. For not impregnated graphite electrode a typical exfoliation behavior is observed with long plateau at ca. 800 mV and lack of any reversible capacity.

Table 1. Basic electrochemical parameters and exfoliation pattern of graphite electrodes in function of the concentration of the impregnation bath; Q_{rev} – reversible capacity in the first cycle, Q_{irr} – irreversible capacity in the first cycle, Eff – coulombic efficiency in the first cycle

Electrode impregnation bath	Q_{rev} / mAh g^{-1}	Q_{irr} / mAh g^{-1}	Eff / %	Exfoliation phenomena
Not impregnated	0	"∞"	0	Total exfoliation
10% siloxane	18	760	2	Partial exfoliation
50% siloxane	244	340	42	Partial Exfoliation
100% siloxane	280	118	70	Lack of visible exfoliation

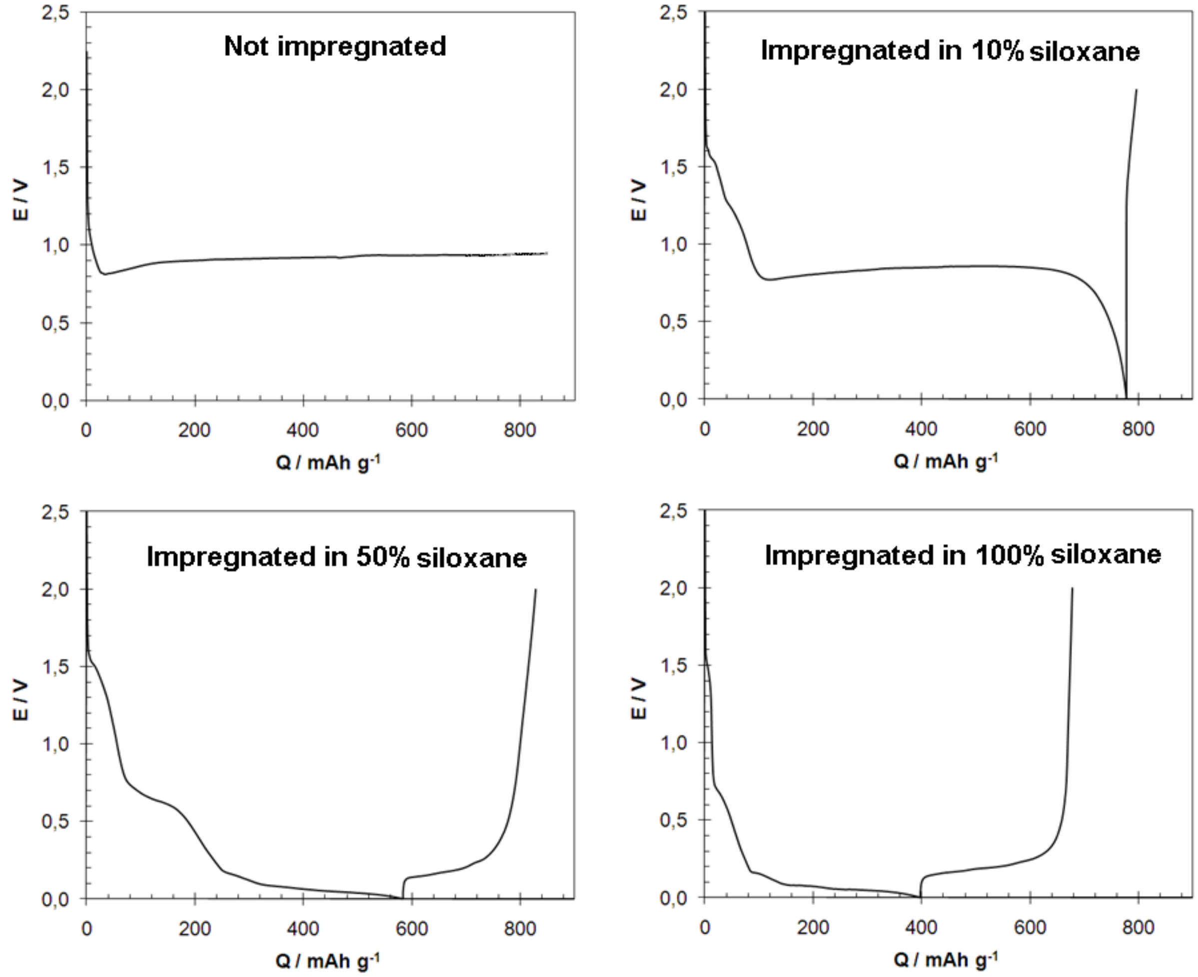


Figure 2. Galvanostatic charge/discharge characteristics of graphite electrodes in function of the concentration of the impregnation bath

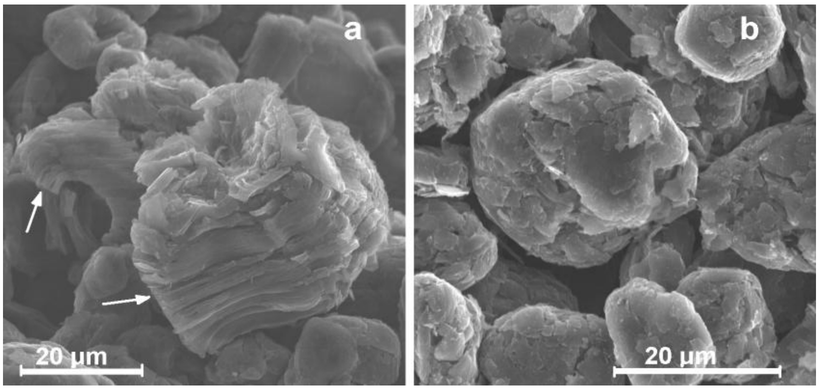


Figure 3. Post-mortem SEM pictures of graphite electrodes: a) not impregnated and b) impregnated in 100% siloxane

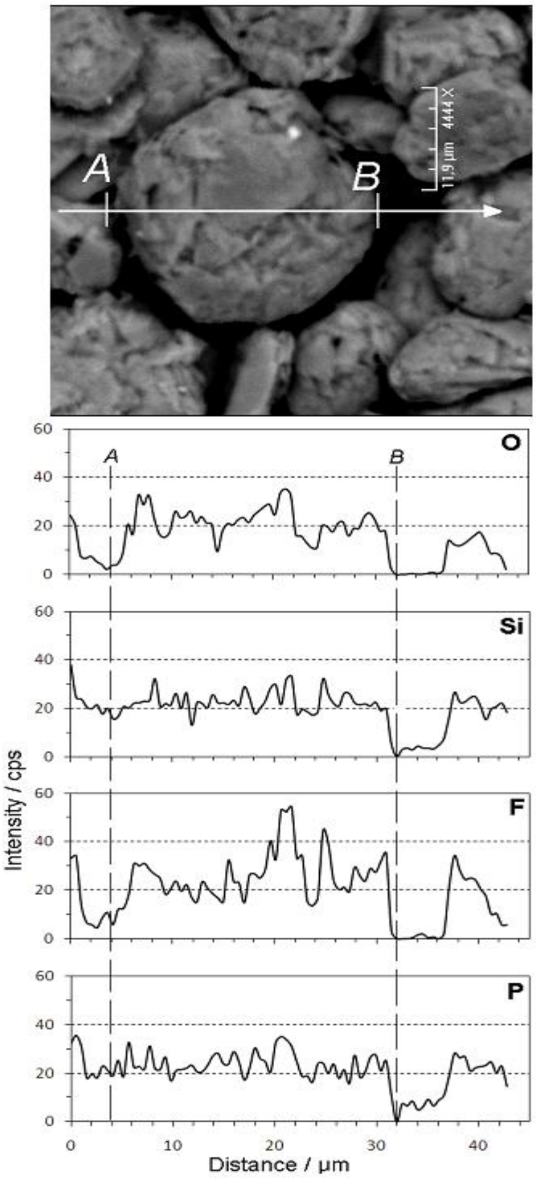


Figure 4. EDX profiles recorded for four key elements on the graphite flake surface along the line indicated on the SEM image; A and B points correspond to the flake edges.

All the electrical charge delivered to the electrode is irreversibly consumed on the continuous decomposition of electrolyte species in contact with progressively created fresh graphite surfaces when the flakes undergo distortion and splitting. The result is also clearly visible on post-mortem SEM image (Fig. 3 a; arrows indicate exfoliation-like morphology). As can be seen in Fig. 2, impregnation in the siloxane agent makes qualitative and quantitative progress, both in terms of the shape of electrochemical characteristics and the recorded capacities. Starting from the dilute impregnation bath a reversible capacity appears, yet negligibly small for 10% siloxane in acetonitrile (18 mAh g^{-1}, see Table 1), but progressively evolving up to 280 mAh g^{-1}, a value approaching practical parameters expected for graphites in conventional electrolytes. Together with increasing reversible capacity, irreversible capacity (defined as the difference between discharge and charge capacities in the first cycle) diminishes from the apparent infinity for not impregnated electrode to a much more reasonable value of 118 mAh g^{-1} (which corresponds to the coulombic efficiency of 70%) for the electrode impregnated in pure siloxane. SEM image proves directly that exfoliation has been totally suppressed in the later case (see Fig. 3 b).

Post-mortem EDX experiment gives insight into the cause of the apparent exfoliation-suppressing action and confirms that the siloxane agent is indeed involved in this phenomenon. As can be seen in the Fig. 4, a graphite particle surface has been scanned so as to detect species engaged in the formation of solid electrolyte interphase. Fluorine and phosphorus present in the SEI obviously come from the decomposition of $LiFP_6$, while marked signals from silicon and perhaps oxygen within the particle area must result from the reductive decomposition of siloxane layer adhering the graphite surface. Thus it has been m evidenced that siloxane components builds in the SEI and modifies its structure and chemical composition in such a way that PC co-intercalation and flake exfoliation is inhibited.

4. CONCLUSIONS

The aim of this communication was to report a novel method of manufacturing graphite anodes for Li-ion batteries. Impregnation in the examined polyether-functionalized disiloxane appears to be an effective way of avoiding destructive exfoliation of graphite anode in electrolytes based on propylene carbonate solvent. Although the beneficial action of the siloxane seems obvious, the method requires optimization in terms of the impregnation bath composition and soaking time, in order to further approach the maximum theoretical lithium intercalation capacity of graphite structure. After this optimization the proposed technique may have a potential of being applied in practical Li-ion battery technologies. This report should also encourage the research of other SEI-formation additives from the siloxane family.

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