Composition, depth profiles and lateral distribution of materials in the SEI built on HOPG-TOF SIMS and XPS studies

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Abstract

The importance to study separately the composition and properties of the solid electrolyte interphase (SEI) on basal and cross-section planes of graphite particles is demonstrated. The lateral distribution of SEI forming compounds at submicron resolution is presented for the first time. It was found that Li and F are the main constituents of the SEI cross-section. The SEI on the solution-side surface of the basal plane contains much more organic materials than that of the cross-section one. The SEI on the HOPG can be described as non-homogeneous. The SEI cross-section is dominated by Li and F, with one to several dozen micron-sized regions where Li and F are almost absent. The distribution of C_2H (and other C_xH_y-based fragments), O, $C_2H_3O_2$ (59), and C_2H_3O (43), shows full coverage and is fairly homogeneous. The true lateral size of the microphases is about 1 μm. TOF SIMS measurements provide direct evidence for the existence of polymers in the basal SEI. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is now well established that in Li-ion batteries containing liquid or polymer electrolytes lithium begins to intercalate into the graphite anode in the first charge in parallel with the formation of a passivating layer, named the Solid Electrolyte Interphase (SEI) [1,2]. At the electrode surface during first charge process there is a competition among many reduction reactions of salts, solvents and impurities, the rates of which depend on i_0, η for each process and catalytic properties of the carbon surface. Reduction of salt anions results in the formation of inorganic precipitates, such as LiF, LiCl, Li_2O. Partial or complete reduction of solvents produces Li_2CO_3, semicarbonates, alkoxides and polymeric compounds. The thickness, the chemical composition and the voltage of the SEI formation depend strongly on the electrolyte composition, temperature, charge–current density and the type of carbon or graphite [1,2].

In most SEI models [3–5], the structure of SEI was represented as consisting of two or more separate layers of different composition and properties. In our recent SEI

study, based on the analysis of the rate constants of the reactions of solvated electrons with electrolyte components, we supposed that reduction of salt anions and solvents proceed simultaneously and both organic and inorganic materials precipitate on the electrode as a mosaic of micro-phases [6,7]. These phases may, under certain conditions, form separate layers, but we believe that it is more appropriate to treat them as polyhetero microphases. We proposed for SEI-electrodes, equivalent circuits, which take into account the contribution of grain-boundary between micro-phases and other interfacial impedance terms. This model accounts for a variety of different types of Nyquist plots data reported for lithium and Li_xC_6 electrodes in liquid non-aqueous and polymer electrolytes. Lithium oxide and lithium fluoride microphases, as the most thermodynamically stable versus lithium, precipitate directly onto the surface. In the solid phase Li_2CO_3 is thermodynamically unstable with respect to lithium and it is expected not to appear onto the electrode surface, but to be reduced to Li_2O and Li_2C [6,7]. The outer SEI part in addition to inorganic precipitates should consist of semicarbonates and polymers (or oligomers, typically polyolephines), which are the products of solvents reduction. Polyolephines are ion non-conducting substances and their content in the SEI is an important issue. On the one hand, they can add flexibility to

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the SEI and being the soft materials can fill void volumes. On the other hand, excessive polymer content can block lithium migration in the SEI. Polymers may cause uneven current distribution and uneven lithium intercalation. At elevated temperatures, polymers and other organic materials may dissolve, leading to discontinuity in the SEI and to a thermal runaway.

Many efforts were undertaken to detect polymers in the SEI, however, the experiments based on FTIR measurements failed. Continues production of active alkyl radicals in electrolyte during first lithium intercalation was detected by Endo [8] with the use of electron-spin resonance method (ESR). Evidence for hydrocarbons in the SEI was found with SIMS analysis in [9].

Lithium intercalation takes place through the cross-section of the graphite. As deduced from many experiments [7,10] the SEI functions differently on the different planes of graphite particles: on the basal plane, it is enough to have an electronic non-conducting film, while on the cross-section (zig-zag and armchair planes) the SEI must also be a good lithium conductor. The different SEI functioning can be reflected in a composition difference. Therefore, it is important to study separately the composition and properties of the SEI on these two planes (basal and cross-section). Carbon atoms on the cross-section zig-zag and arm chair planes were found to be much more active than carbon atoms on the basal plane of the glassy carbon and highly oriented pyrolytic graphite (HOPG) [11]. Thus, HOPG, which is considered as a special case of graphite materials analogous to a single crystal, was used as a model electrode in our study.

Preliminary results using TOF SIMS at low resolution were recently published [12] and direct evidence for the existence of polymers in the SEI was found.

The goals of our work were: to study separately the composition of the SEI on the different planes of the HOPG formed in $LiPF_6$–EC:DEC (1:1) solutions with the use of TOF SIMS and XPS techniques and to provide details of the SEI microphase morphology at the micron size level.

2. Experimental

HOPG type ZYH 2 mm × 12 mm × 12 mm 3.5° Mosaic spread samples (Advanced Ceramics Corporation) were cut into two 2 mm × 6 mm × 12 mm blocks. The HOPG surface was freshly prepared prior to each experiment by cleaving with an adhesive tape. Then, they were washed by AR *iso*-propanol, acetone and distilled water. The SEI was formed on HOPG in flooded Li/HOPG cells. These cells consisted of a HOPG electrode supported by a nickel screen, a lithium foil supported by a nickel grid, Celgard 2400 separator, and EC:DEC (1:1) 1 M $LiPF_6$ electrolyte. The HOPG cells were discharged at 0.5 and 1 mA/cm² until their voltage fell to 0.2 V and then at 0.23 mA/cm² until 0.01 V. They were charged back (deintercalation) at 0.05 mA/cm² until their voltage reached 2.5 V. After being washed with

DMC and vacuum dried they were analyzed with the use of XPS and TOF SIMS. XPS measurements were performed in UHV (2.5×10^{-10} Torr base pressure) with the use of a 5600 Multi-Technique System (Physical Electronics Inc., USA) with a monochromatic Al Kα source (1486.6 eV). The depth profile was obtained by argon ion sputtering, at a sputtering rate of 0.5 nm/min based on a SiO_2/Si sample. TOF SIMS tests were performed (on samples intercalated at 1 mA/cm², procedure b) with the use of TRIFT II (Physical Electronics Inc., USA) at the following operating conditions: primary ions In^+, dc sputtering rate 0.035 nm/min based on SiO_2.

3. Results and discussion

In order to obtain the information on the chemical composition of the SEI and the depth distribution of the SEI forming materials, high-resolution XPS spectra were recorded at different time of sputtering. The intensity, the shape and the position of the main peaks at C 1s and O 1s spectra of the cross-section and basal SEI were found to change on sputtering, indicating different SEI composition on the solution-side surface, in the bulk and at the bottom. Using least square curve fitting technique the carbon peaks were assigned to Li–O–C, C–O–C, C–OH and C=O groups. The oxygen peaks were related to Li–O–C, C–O–C, C–OH, C=O, LiOH and Li_2O components. After deconvolution procedure [10] the depth profiles of the cross-section and basal SEI forming compounds were constructed. The main constituent of the SEI cross-section is LiF (about 90 at.% in the bulk) with some polymers (polyolephines and oxygen-bound polymers) at the solution side of the SEI and some LiOC groups that may be attributed to alkoxides. It should be mentioned that lithium carbonate was found neither on the solution side surface of the SEI cross-section, nor in the bulk of it. Li_2O is present only at the bottom of the SEI.

The distinctive feature of the basal SEI is the presence of 10–30 at.% Li_2CO_3 on the surface and in the bulk. The basal SEI contains much less LiF and much more polymeric materials (about 50% at the surface of the SEI). Thus, it can be concluded that on the basal plane, the greatest contribution to the SEI formation is solvent reduction, whereas on the cross-section it is the reduction of electrolyte anions. Alkoxides and Li_2O were found in the bulk and at bottom of the basal SEI. A dramatic increase of the carbon signal arising from the HOPG underlying the basal SEI was observed at about 2 nm depth, while for the cross-section one the HOPG carbon signal was seen at about 30 nm. This unambiguously points to the fact that the basal SEI is thinner than the cross-section one.

In interpreting the concentration XPS depth profile it should be remembered that the sputtering efficiency depends on the type of material, it may be higher for organic materials and lower for stable inorganic materials. Some material decomposition and surface chemical reactions are to be expected. These factors may affect to some extent the

concentration depth profile, but in our opinion would not change it drastically.

TOF SIMS measurements were carried out for the first time at the 1 μm lateral resolution for SEI study on the different planes of HOPG. According to the time of flight secondary ion mass spectra Li, F, O, C and H containing fragments were found in the SEI built on both the cross-section and basal planes. However, a number of counts recorded at each mass from different HOPG planes were significantly different. For instance, the normalized Fluor intensity (number of F counts divided by a total number of secondary ion counts and multiplied by 10^5) was 26,563 for the SEI cross-section and 6065 for the basal. The normalized intensity for CH species was 3120 and 12,992, respectively. Thus, it is clear that Li and F dominate the cross-section of the SEI spectrum and organic species dominate the basal one in a good agreement with the XPS data. The solution side surface of the basal-SEI is very rich in C_2H_3O. The normalized intensity of C_2H_3O is four times that of Li indicating that most of it cannot be bound to LiOC groups
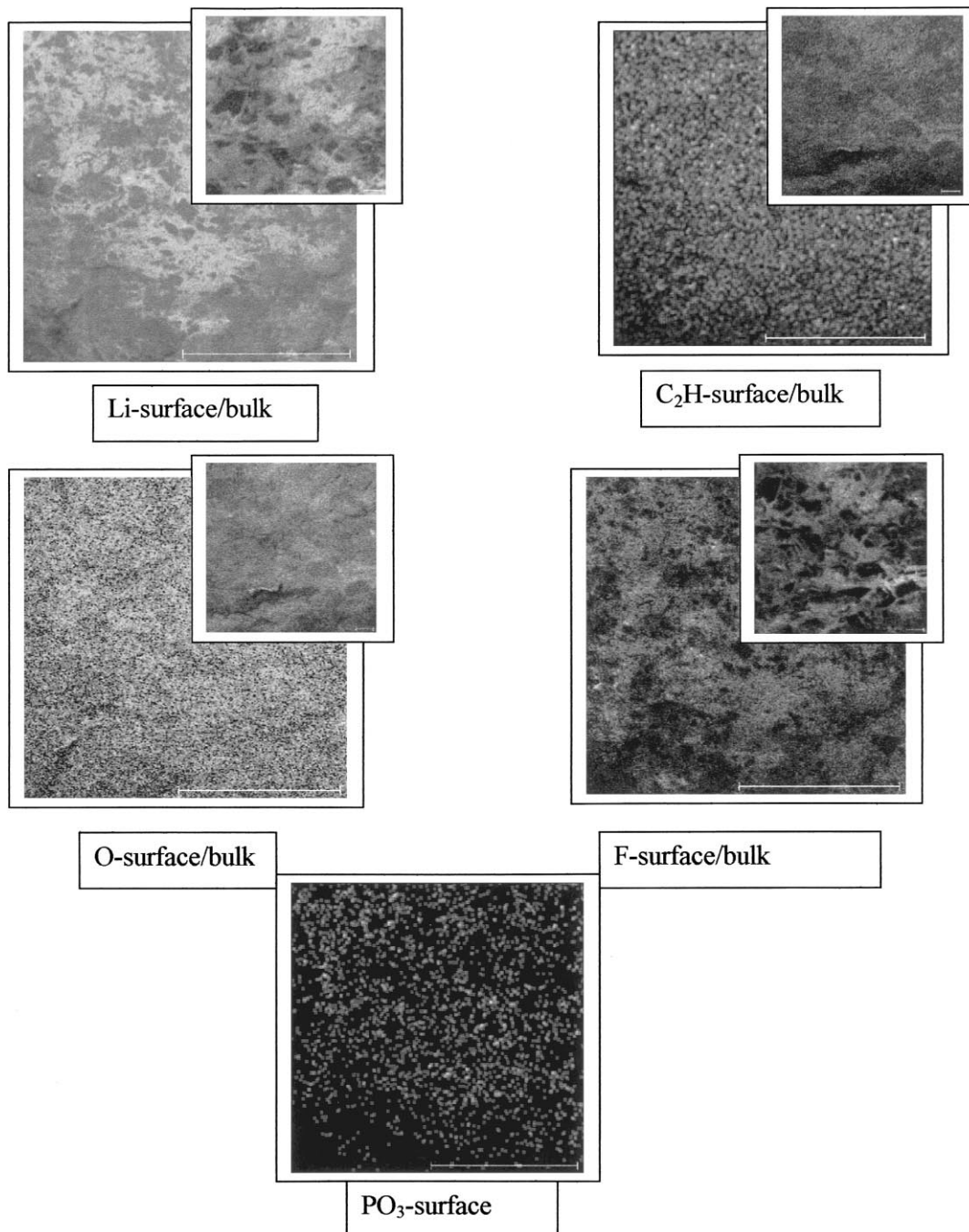

Fig. 1. TOF SIMS ion images of the surface and bulk SEI on the HOPG cross-section.

in alkylcarbonates or alkoxides. We suggest assigning the excess of $C_2H_3O_2$ fragments to polymers containing oxygen groups. Heavy fragments represented by masses 280.023 and 144.707 were found only at the surface of the SEI.

From the depth profiles we attempt to estimate roughly the SEI thickness. Similar to the XPS tests it should be recognized that in TOF SIMS measurements molecular species can be damaged and fragmented when sputtered. Thus, the depth profile of organic materials may represent their destruction with time and not only their concentration versus depth. The apparent SEI thickness was calculated by taking the depth at half signal intensity. The intensity of secondary ion counts of all species decays to one-half of its maximum

value in about 0.5–2.5 nm at the basal plane and in about 1.7 to more than 30 nm (for F) at the cross-section. The secondary ions signal of the same species decays 1.7–5.5 times (or more) faster at the basal plane than at the cross-section. SEI thickness measured by XPS for SEI formed under similar conditions is 7 nm for basal-SEI and 35 nm for cross-section SEI. Thick SEI at the cross-section was generally explained by solvent cointercalation and exfoliation of the graphite [13–16]. This must be followed by formation of carbonates as a result of solvent reduction. However, carbonates were not found either on the solution-side surface, or in the bulk of the cross-section SEI. Contrary to the cross-section SEI, the bulk SEI contains up to 30 at.% of
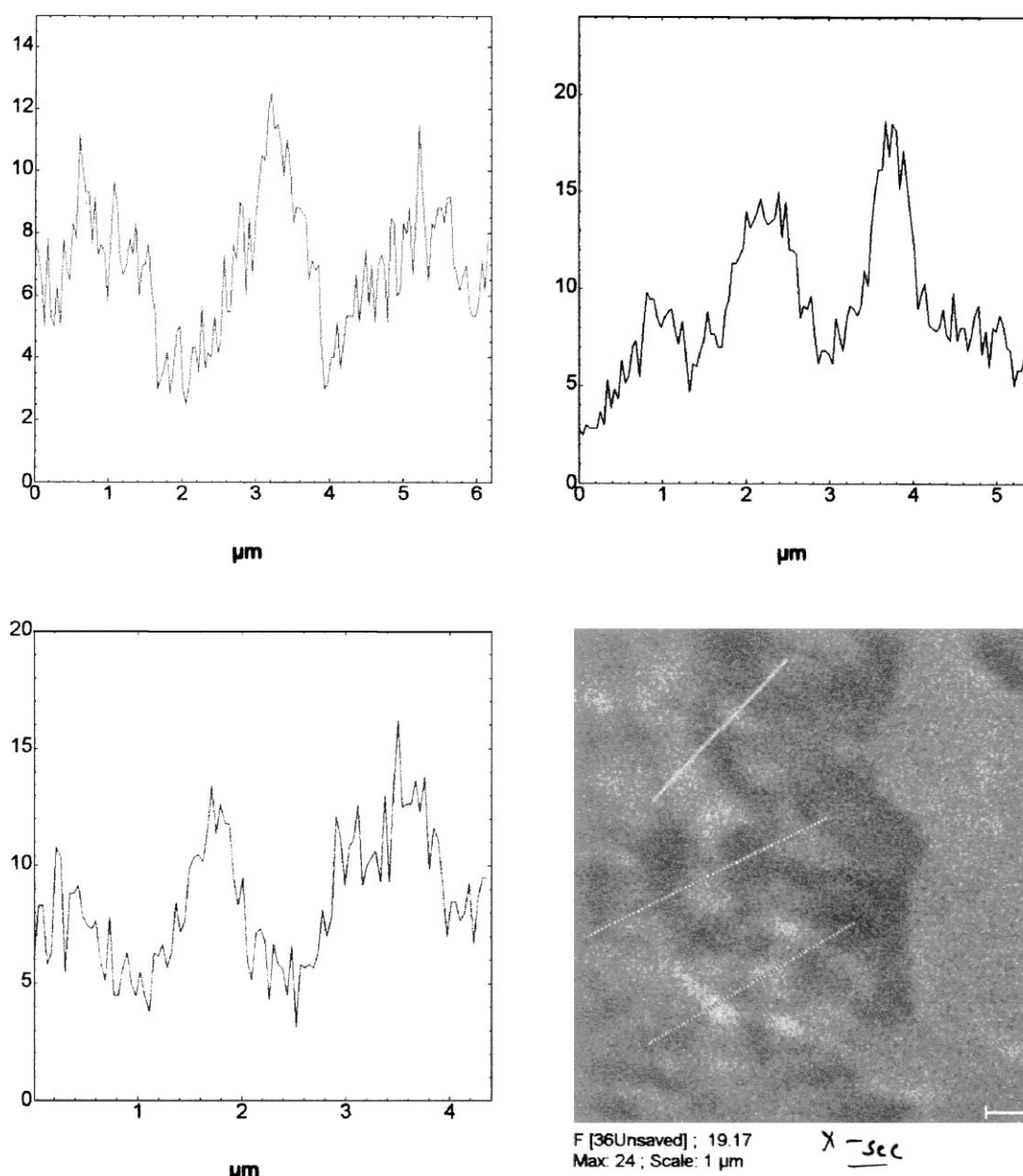

Fig. 2. TOF SIMS fluor image and lateral size profiles of the SEI forming microphases.

lithium carbonate. Therefore, its absence in the cross-section SEI cannot be explained only by the reduction of Li_2CO_3 to alkoxides. XPS data showed that the major cross-section SEI compound is LiF (up to about 90 at.% (excluding H atoms) in the bulk). The normalized counts of PO_3^- species recorded by TOF SIMS at the cross-section is about three times higher than at the basal plane. These two findings clearly prove that the exchange current density (i_o) for $LiPF_6$ (and for HF) reduction is much higher at the cross-section than it is at the basal plane. We believe that this is the reaction that determines the cross-section SEI composition. The increased thickness of the cross-section SEI as compared to the basal one may be explained by the cointercalation of ion aggregates like $Li_2PF_6^+$ in the beginning of SEI formation. This is followed by $Li_2PF_6^+$ reduction to PO_3^- species detected by the TOF SIMS. Possible coinercalation of protons as products of HF dissociation cannot be excluded also. Partial exfoliation of graphite by $Li_2PF_6^+$ and hydrogen penetration may cause increasing of the SEI thickness.

The appearance of large number of counts of C and CH species especially at the basal plane supports previous claims for the existence of polymers in the SEI. The most convincing evidence is the CH_2 sequence found on the basal plane. A sequence of masses: 311, 325, 339, 353, 367 which differ by one CH_2 group can be assigned to our opinion to polyolefins $(CH_2)_n$ without a doubt.

In our recent model of the SEI structure it was supposed that the SEI consists of polyheteromicrophases. For the first time the lateral distribution of materials in the SEI was measured by TOF SIMS at about 1 μm lateral resolution. Fig. 1 depicts surface and bulk ion images for the SEI on the basal and on the cross-section planes. The brighter is the image, the larger is the number of secondary ion counts recorded at the corresponding mass fragment. The main conclusion to be gained from the analysis of the images is that the SEI on the HOPG has non-homogeneous chemical structure. The SEI on the cross-section is dominated by Li and F, with one to several dozen micron-sized regions where Li and F are almost absent. The distribution of C_2H (and other C_xH_y-based fragments), O, $C_2H_3O_2$ (59), and C_2H_3O (43), show full coverage and is fairly homogeneous. PO_3 species are distributed as small few micron-size icelands. Taking into account that all TOF SIMS images were recorded almost simultaneously from the same region, we can conclude that there is an overlap of Li and F arrangements with those of the organic species indicating an intimate mixture of these species at the submicron level. The chemical structure of the SEI after sputtering has remained unaltered in general. However, for some organic and oxygen-containing fragments, that showed full and homogeneous coverage on the solution-side surface of the SEI the bulk distribution is non-uniform (see inserts).

The SEI on the basal plane is dominated by homogeneously distributed organic materials (some contain oxygen, C_2H_3O has the highest contribution). Li and F are concentrated in large regions (100 μm), with some smaller micron

sized particles. There is little or no correlation with graphite topography.

To get more precise information of the lateral size of SEI forming microphases we analyzed several different areas marked by coloured solid lines of the cross-section SEI at 1 μm lateral resolution. The corresponding plots represent the number of secondary ion counts recorded along each line as a function of distance. As can be seen from Fig. 2 the true lateral size of the SEI microphases is about 1–2 μm.

In order to correlate the composition and morphology of the SEI formed on the HOPG and on the real anode in lithium-ion batteries we perform the TOF SIMS SEI characterization on the SPG-20 electrode. The data will be published soon.

4. Summary

The lateral distribution of SEI materials was determined for the first time (at about 1 μm lateral resolution) with the use of TOF SIMS. The true lateral size of the microphases is about 1 μm. The SEI on the HOPG can be described as non-homogeneous. The SEI on the cross-section is dominated by Li and F. The SEI on the basal plane is dominated by organic materials. TOF SIMS measurements provide, for the first time, direct evidence for the existence of polymers in the basal SEI. Heavy organic fragments were found mainly at the surface of the basal SEI. The thickness of the SEI on the basal plane was found to be (by both XPS and TOF SIMS) three to five times smaller than that on the cross-section.

Acknowledgements

References

[1] E. Peled, J. Electrochem. Soc. 126 (1979) 2047.
[2] E. Peled, in: J.P. Gabano (Ed.), Lithium Batteries, Academic Press, New York, 1983, p. 43.
[3] J.G. Thevenin, R.H. Muller, J. Electrochem. Soc. 134 (2) (1987) 273.
[4] D. Aurbach, I. Weissman, A. Zaban, O. Chuzid (Youngman), Electrochim. Acta 39 (1994) 51.
[5] K. Kanamura, H. Tamura, S. Shiraishi, Z.-i. Takehara, J. Electroanal. Chem. 394 (1995) 49.
[6] G. Ardel, D. Golodnitsky, E. Peled, J. Electrochem. Soc. 144 (1997) L208.
[7] E. Peled, D. Golodnitsky, J. Penciner, in: J.O. Besenhard (Ed.), Handbook of Battery Materials, Wiley-VCH, New York, 1999, p. 419.
[8] E. Endo, M. Ata, K. Sekia, K. Tanaka, J. Electrochem. Soc. 146 (1999) 49.
[9] K.R. Zavadil, R.A. Guidotti, W.R. Even, Mat. Res. Soc. Symp. Proc. 496 (1998) 539.
[10] D. Bar-Tow, E. Peled, L. Burstein, J. Electrochem. Soc. 146 (824) (1999) 11.

[11] McCreery, Interfacial Electrochem, 1999.

[12] E. Peled, D. Bar Tow, A. Merson, L. Burstein, Microphase structure of SEI on HOPG, J. New Mater. Electrochem. Systems 3 (2000) 321.

[13] J.R. Dahn, et al., in: G. Pistoia (Ed.), Lithium Batteries, New Materials, Development and Perspectives, Elsevier, New York, 1994, p. 22.

[14] B. Simon, J.P. Boeve, B. Spigi, B. Broussely, Abstract 156, Electrochem. Soc. Int. Soc. Electrochem. Meeting Abstract 97 (2) (1997).

[15] M. Inaba, Z. Siroma, Y. Kawatate, A. Funabiki, Z. Ogumi, J. Power Sources 68 (1997) 221.

[16] J. Besenhard, M. Winter, J. Yang, W. Biberacher, J. Power Sources 54 (1995) 228.