

# In situ characterization of the SEI formation on graphite in the presence of a vinylene group containing film-forming electrolyte additives

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Dedicated to Prof. H.J. Schäfer's 65th birthday

## Abstract

Acrylic acid nitrile (AAN) is introduced as a novel example out of the large class of vinylene groups containing film-forming additives for lithium-ion batteries. The electrochemical behaviour, especially the electrolyte additive reduction and the associated film formation in the presence of this compound is investigated with the in situ methods of Fourier transform infrared (FT-IR) spectroscopy and electrochemical quartz crystal micro balance (EQCM). The results clearly point at a solid electrolyte interphase (SEI) formation mechanism, which proceeds via the cathodically induced polymerization of AAN. We suggest that the electro-polymerisation of vinylene groups is a main electrolyte reduction mechanism for a vinylene group containing electrolyte additives. The outstanding filming properties of vinylene compounds such as AAN allow the use of graphitic carbon anodes in PC-based electrolytes even when only 1% of the additive is present in the electrolyte.

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## 1. Introduction

The formation of polymeric products is an often-observed phenomenon in electroorganic chemistry. The precipitation of thin polymer layers on the electrode is, for instance an undesired side-effect occurring during preparative synthesis of many organic compounds. The formed polymer may be insoluble and thus cover the electrode. Well-known examples are the vinylene monomers, which can be polymerized by electrochemically induced reduction or oxidation. The basic principle of an electrochemically induced reduction process (cathodically induced electro-polymerisation) of vinylene compounds is shown in Fig. 1. The vinylene monomers are dissolved in an electrolyte system. During reduction, the first step is the electron transfer from the electrode, which starts a chain reaction via addition of the formed reactive species (in this case a radical anion) to the double bonds of other monomers (shown in Fig. 1) or other solvent components present in the electrolyte. Only

the first electron transfer step is an electrochemical one, thus a charge-consuming step. The subsequent steps are of a chemical nature.

An example of vinylene monomers, which has been very often investigated in organic electrochemistry, is the acrylic acid nitrile (AAN,  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$ ) [1]. Understanding the electro-polymerisation of this compound gives important information to the optimization of the technical electro-synthesis of adiponitrile. This Monsanto process [2] is one of the most famous and important technical applications of an electro-polymerisation reaction, the formed adiponitrile being a precursor for the production of Nylon<sup>®</sup>.

The best current yields of polymerization (ratio of the number of monomers, which have been transformed to polymer units, per number of transferred electrons) are obtained in dry, i.e. water-free solvents [3]. The yields may reach 1000%, i.e. 10 monomers are polymerized by the transfer of only one electron from the electrode to the solution.

The effectiveness of the reaction, the barely charge-consuming polymerisation mechanism and the applicability of the reaction in nonaqueous solvents, strongly suggests the use of this reaction mechanism as a general strategy for the

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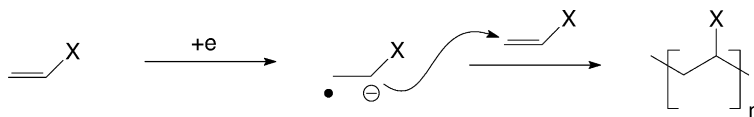


Fig. 1. Cathodic, i.e. by reduction induced polymerization of vinylene monomers.

controlled formation of protective solid electrolyte interphase (SEI) films on graphite anodes in lithium-ion batteries. As the network formed from the polymer chains on the surface (Fig. 2) has a predominantly organic character, i.e. can be penetrated by the organic electrolytes typically used in lithium-ion batteries, one may assume SEI formation underneath the polymer network. This can be quite favourable as the formed SEI products are hindered by the network to diffuse into the bulk electrolyte and are therefore kept close to the surface. As a consequence, the formation of a rapidly formed, effective SEI can be expected. On the other hand, the polymer formed on the surface may itself act as a part of the SEI as well.

Graphitic carbons are widely used as negative electrode materials in lithium-ion batteries. If propylene carbonate (PC) is used as the main electrolyte solvent, graphite exfoliation initiated by intercalation of PC-solvated lithium ions occurs [4]. This reaction can be suppressed by a SEI on the graphite surface, which is permeable only to unsolvated lithium ions, and which is established before PC cointercalation takes place. Several electrolyte components, in particular film-forming electrolyte additives are well known to create such an effective SEI [5]. As a pure PC-based electrolyte is not compatible with graphite at all, it can be considered as a tough base electrolyte for the test of the filming capabilities of electrolyte additives.

Here, we show how vinylene group-containing compounds such as AAN can be used as effective electrolyte additives in PC-based electrolytes even with graphitic car-

bon anodes. We will illustrate the reductive decomposition and the associated SEI formation mechanisms on carbon anodes in the presence of the additive by means of in situ Fourier transform infrared (FT-IR) spectroscopy and in situ electrochemical quartz crystal microbalance (EQCMB).

## 2. Experimental

PC (Merck or Honeywell, battery grade),  $\text{LiClO}_4$  (Mitsubishi Chemical Corp., battery grade) and acrylic acid nitrile (Aldrich) were used as received. Lithium bis(trifluoromethane sulfonyl) imide ( $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ , LiTFSI, 3 M) was dried with a turbo molecular pump in vacuo at  $140^\circ\text{C}$  for 5 days. Graphite-based anodes were made from TIMREX<sup>®</sup> SFG 44 and KS 6 synthetic graphites (Timcal Group). All electrodes contained 5 wt.% of polyvinylidene fluoride (PVdF, Mitsubishi Chemical Corp.) binder.

Electrolyte preparation and cell assembly were accomplished under dry argon atmosphere in a glove box. The water content of the electrolytes determined by Karl Fischer titration was less than 15 ppm. Cyclic voltammetric and constant current charge/discharge experiments were carried out in laboratory type glass cells with lithium counter and reference electrodes and an excess of electrolyte. The electrodes were not closely packed in separator materials but placed in the electrolyte without any further support. Current densities and specific charges are given with respect to the graphite mass.

In situ FT-IR and EQCMB studies were performed in self-developed cells. The FT-IR experimental set-up uses a glassy carbon working electrode, lithium counter and reference electrodes. The cell for the EQCMB measurements was equipped with a quartz crystal coated with KS 6 graphite. Lithium was used as counter and reference electrodes. The electrochemical device was an EG&G PAR potentiostat, type 263A with a frequency analyzer QCA 917.

## 3. Results and discussion

AAN is a typical example of a vinylene group containing electrolyte additives. For the analytical investigations we used a concentration of 5 vol.% AAN added to 1 M  $\text{LiClO}_4/\text{PC}$  electrolyte. Fig. 3 shows an IR spectrum of the PC electrolyte without additive, Fig. 4 shows IR spectra with AAN. During a decrease of the potential of the glassy carbon electrode, a change of the characteristic IR bands was monitored. By taking advantage of the subtractively normalized in

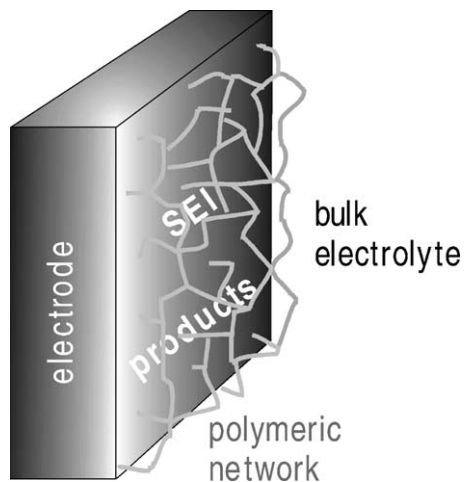


Fig. 2. Formation of a polymeric chain network and retention of SEI products at the electrode surface.

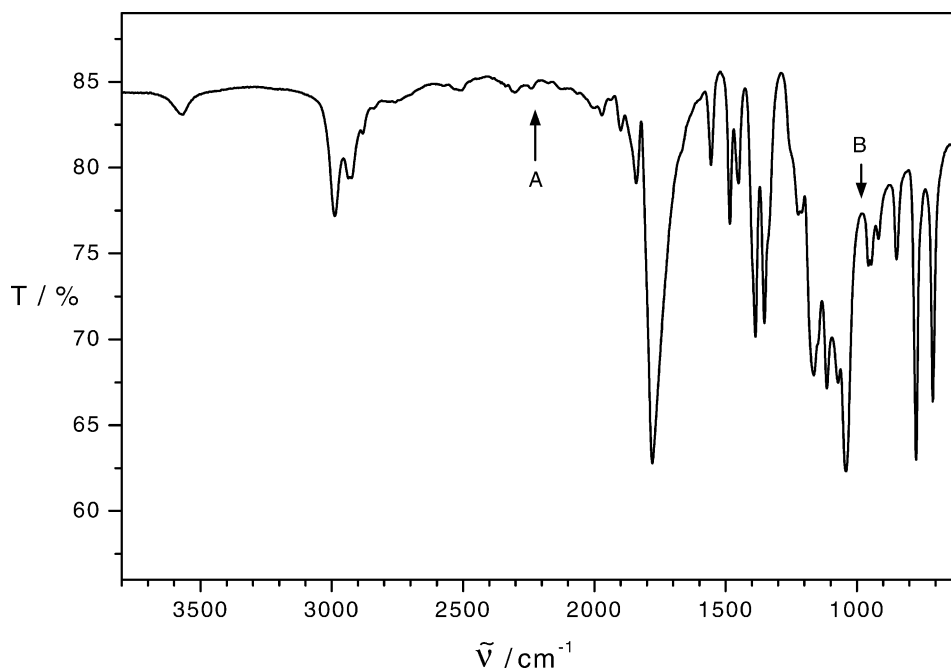


Fig. 3. In situ FT-IR spectrum of 1 M LiClO<sub>4</sub>/PC on a glassy carbon working electrode at OCV; (A) and (B) indicate the absence of characteristic IR bands of AAN.

situ FT-IR spectroscopy (SNIFTIRS) mode, Figs. 5 and 6 show the changes of the three main characteristic IR bands during reduction in more detail. In the SNIFTIRS mode, positive bands indicate a decrease in concentration and negative bands indicate an increase in concentration of the species represented by the peak. All changes in magnitude of the peaks can be associated with the electrochemical

reduction of the additive at the carbon working electrode. The polymerization of the AAN can be tracked via the decrease of the C–H deformation vibration at 975 cm<sup>-1</sup>, which is characteristic for the vinylene group (HC=CH<sub>2</sub>) (Fig. 5), and via the decrease of the C≡N stretching vibration of the unsaturated nitrile at 2225 cm<sup>-1</sup>. Simultaneously, the formation of a saturated C–C bond in the vicinity of a nitrile

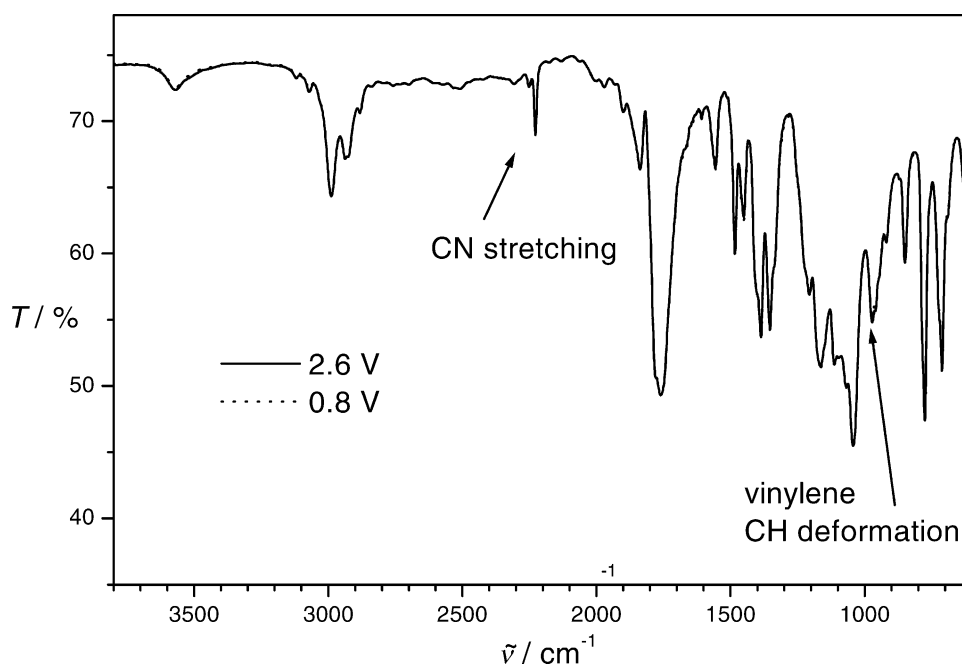


Fig. 4. In situ FT-IR spectra of AAN (5% v/v) in 1 M LiClO<sub>4</sub>/PC on a glassy carbon working electrode at potentials of 2.2 and 0.8 V vs. Li/Li<sup>+</sup>.

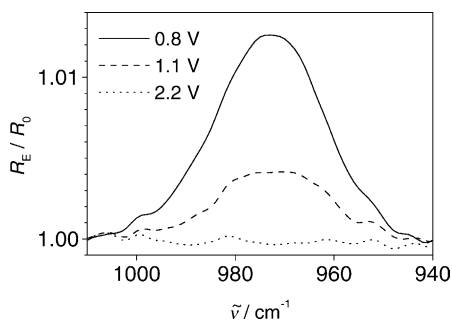


Fig. 5. Subtractively normalized in situ FT-IR spectrum (SNIFTIRS): decrease of the C–H deformation vibration of vinylene compounds ( $975\text{ cm}^{-1}$ );  $R_E$ , spectrum measured at the given potential;  $R_0$ , spectrum measured at open circuit potential.

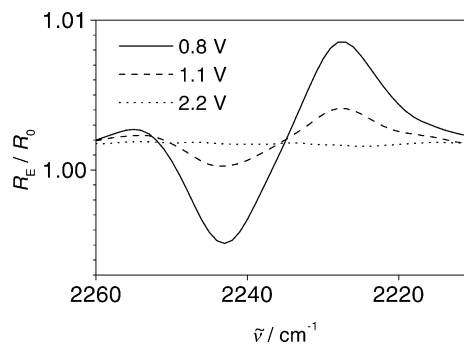


Fig. 6. Subtractively normalized in situ FT-IR spectrum (SNIFTIRS): decrease of the unsaturated ( $2225\text{ cm}^{-1}$ ) and increase of the saturated ( $2245\text{ cm}^{-1}$ ) C≡N stretching vibration of nitriles;  $R_E$ , spectrum measured at the given potential;  $R_0$ , spectrum measured at open circuit potential.

group can be observed, which is represented in the IR spectrum by the C≡N stretching vibration of the saturated nitrile at  $2245\text{ cm}^{-1}$  (Fig. 6). The results clearly confirm the reductive polymerization mechanism proposed in Fig. 1, where first the double bond of the additive is reduced and successively the unsaturated vinylene monomers are converted via a chain reaction into a polymer with saturated C–C bonds.

In order to distinguish between: (i) the formation of soluble and mobile reduction products and (ii) the precipitation of an insoluble and immobile film attached to the electrode surface, the EQCMB method is very useful. In situ EQCMB reveals that the weight changes due to film growth on graphite start at a reduction potential of approximately  $1.3\text{ V}$  versus  $\text{Li}/\text{Li}^+$  (Fig. 7). The film obviously contains polymerisation products of AAN, as we could confirm the presence of nitrogen in the film by X-ray photoelectron spectroscopy (XPS) [5].

An investigation of the electrochemical properties of the SEI films formed in a PC-based electrolyte in the presence of AAN disclosed very good filming capabilities even when AAN is used only in additive amounts of 1 vol.%. The cyclic voltammogram shows a flat, sparsely current-consuming filming process and well resolved intercalation and de-intercalation peaks, indicating a low SEI film resistance. PC intercalation is effectively suppressed. Apparently, a film permeable for lithium ions but impermeable for the solvating PC molecules, is formed at potentials high above the potentials of solvated intercalation (the latter are typically below  $\approx 0.9\text{--}0.7\text{ V}$  versus  $\text{Li}/\text{Li}^+$ ).

Constant current charge/discharge cycling reveals good performance both with regard to discharge capacities and charge/discharge efficiencies (Figs. 8 and 9). Beginning with about 87% efficiency in the first cycle, the values are rapidly reaching close to 100% in the later cycles.

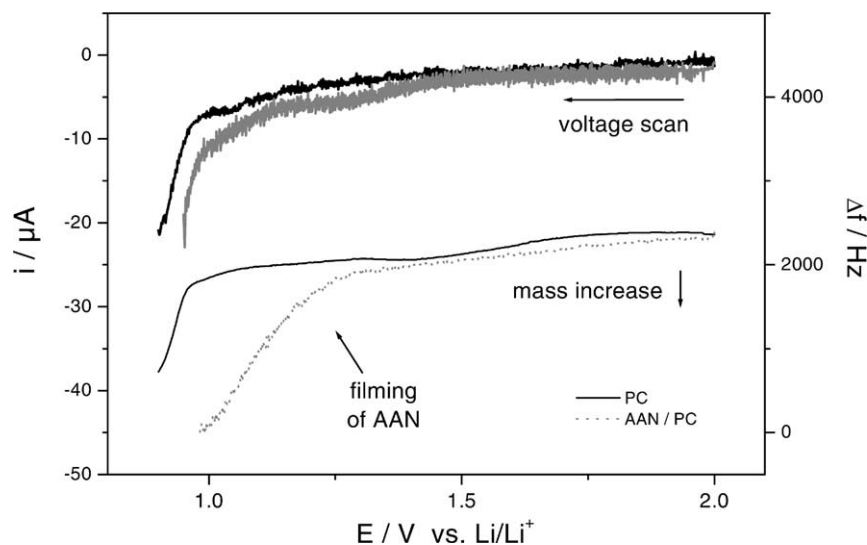


Fig. 7. EQCMB experiment of graphite in PC/1 M  $\text{LiClO}_4$  without (—) and with (···) 5% AAN, scan rate:  $0.2\text{ mV s}^{-1}$ .

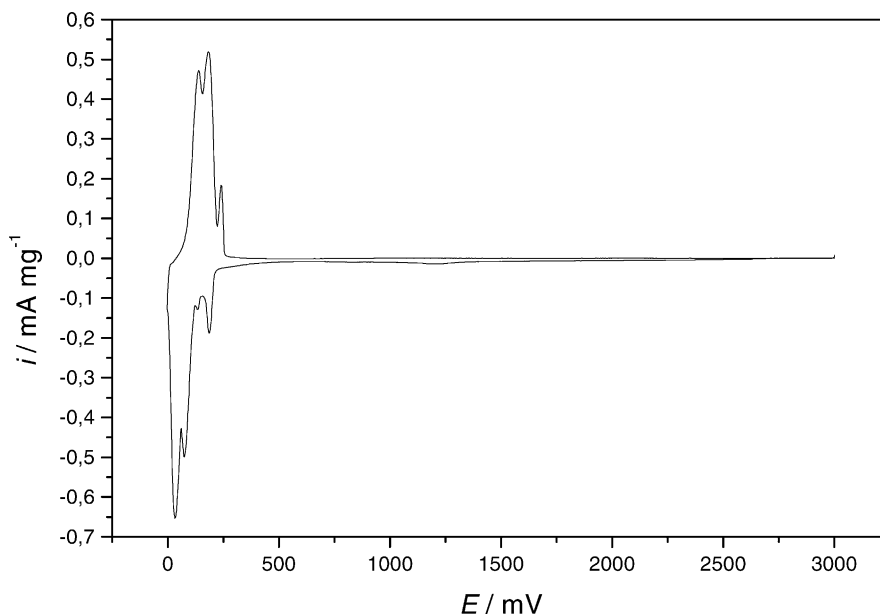


Fig. 8. Cyclic voltammogram of a graphite composite electrode (TIMREX KS 6), in 1 M  $\text{LiN}(\text{SO}_2\text{CF}_3)_2 + \text{PC/AAN}$  (99:1, v:v), scan rate  $0.05 \text{ mV s}^{-1}$ ; V vs.  $\text{Li/Li}^+$ ; counter/reference electrode: lithium.

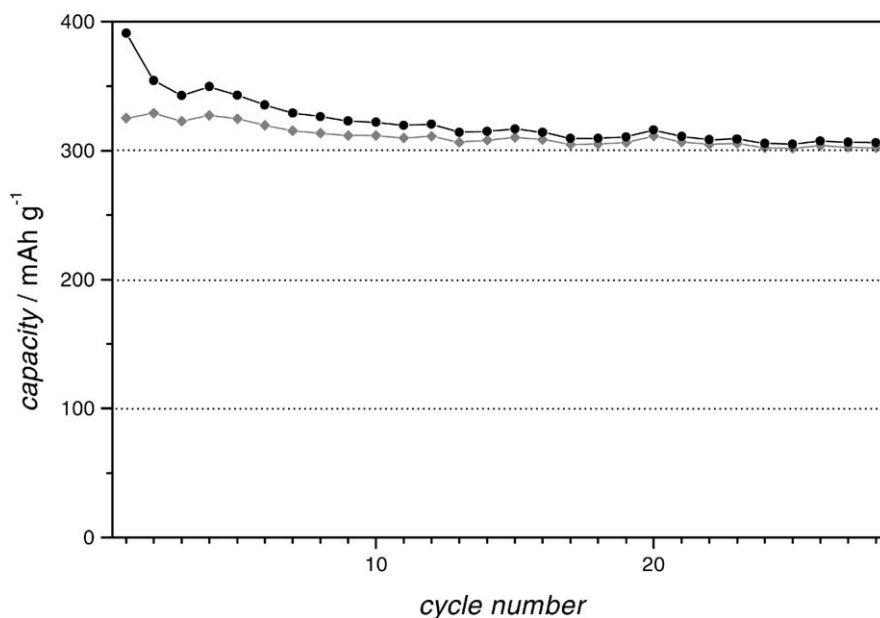


Fig. 9. Charge (●) and discharge (◆) capacities of a graphite composite electrode (SFG 44), in 1 M  $\text{LiN}(\text{SO}_2\text{CF}_3)_2 + \text{PC/AAN}$  (99:1, v:v); current/cut-off conditions:  $-100 \mu\text{A mg}^{-1}/52 \text{ mV} // -20 \mu\text{A mg}^{-1}/24 \text{ mV} // 100 \mu\text{A mg}^{-1}/255 \text{ mV} // 20 \mu\text{A mg}^{-1}/1500 \text{ mV}$  vs.  $\text{Li/Li}^+$ ; counter/reference electrode: lithium.

#### 4. Conclusions

Vinylene compounds are very promising for use as film-forming electrolyte additives in lithium-ion batteries. They are commercially available in a big variety and at low costs. The vinylene additive presented in this study, AAN is a typical example for this group of additives. It shows a beneficial filming behaviour on graphite, even in combination with a propylene carbonate-based electrolyte, resulting in

excellent anode cycling stability. Having in mind that only 1% of an additive is required for a sufficient film formation and 99% of the electrolyte can be chosen independently, an impressive scope for the development of optimized electrolytes is achieved. Lithium-ion batteries with graphitic anodes may be no longer strongly dependent on the currently used ethylene carbonate (EC), which is considered to be indispensable because of its excellent SEI filming properties, but which is a solid at room temperature (melting point  $36 \text{ }^\circ\text{C}$ , as

EC has to be used in amounts of 25–50 vol.%, the low temperature performance of the battery inevitably suffers).

It is also conceivable to use compounds with polymerizable double bonds for the formation of polymeric films at cathodes. The oxidation or reduction potentials can be simply adjusted via the substitution pattern at the double bond, e.g. by using different functional groups “-X” (cf. Fig. 1). The establishment of SEI-like interphases for protection of the cathode against dissolution or the formation of shut-down films at the cathode surface as protection against overcharge will certainly be an important application for the polymerizable electrolyte additives. The design of electrolyte salts, solvents and additives which can be combined in a way that very specific requirements on the electrolyte are fulfilled, such as good low temperature performance, high temperature stability, low flammability, good wetting ability, overcharge protection, etc. will be crucial to the future development of “functional electrolytes”.

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## References

- [1] M.M. Baizer, J.D. Anderson, *J. Org. Chem.* 30 (1965) 1351.
- [2] Monsanto, US Patent No. 3,375,237 (1964).
- [3] O.F. Olaj, J.W. Breitenbach, B. Buchberger, *Angew. Makromol. Chem.* 3 (1968) 160.
- [4] J.O. Besenhard, *Carbon* 14 (1976) 111.
- [5] H.J. Santner, K.-C. Möller, J. Ivanko, M.G. Ramsey, F.P. Netzer, S. Yamaguchi, J.O. Besenhard, M. Winter, *J. Power Sources*, this volume.