

AFM study of surface film formation on a composite graphite electrode in lithium-ion batteries

Soon-Ki Jeong^{a,b}, Minoru Inaba^{c,*}, Yasutoshi Iriyama^b,
Takeshi Abe^b, Zempachi Ogumi^b

^aJapan Science and Technology Corporation, Kawaguchi-shi, Saitama 332-0012, Japan

^bDepartment of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

^cDepartment of Molecular Science and Technology, Faculty of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

Abstract

An in situ electrochemical atomic force microscopy (AFM) observation of a composite graphite electrode surface was performed in 1 mol dm⁻³ LiClO₄ dissolved in a mixture of ethylene carbonate (EC) + diethyl carbonate (DEC), and propylene carbonate (PC) to show the applicability of scanning probe microscopy (SPM) to studies using composite graphite electrodes. In EC + DEC, three kinds of morphological changes (curling, swelling, and exfoliation) in the vicinity of the particle edges were observed in the potential range of 0.8–1.4 V versus Li⁺/Li. These morphological changes were caused by the intercalation of solvated lithium ions and their subsequent decomposition between graphene layers. On the other hand, vigorous exfoliation and rupturing of graphene layers of the graphite particles were observed at 0.9 V in PC. In addition, deterioration by the formation of holes in the composite graphite electrode was observed in PC, which is attributable to gas evolution upon decomposition of PC molecules.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Composite graphite electrode; Scanning probe microscopy; Lithium-ion batteries

1. Introduction

The surface film, which is formed on graphite negative electrodes during the initial charging and often called the solid electrolyte interphase (SEI), is a key component in lithium-ion batteries [1]. The battery reactions, electrochemical lithium intercalation and de-intercalation, are strongly affected by the nature of the surface film. Understanding the mechanism for surface film formation is thus very important, and has been a focus of much work over the past decade.

Since the first introduction of an in situ technique using scanning tunneling microscopy (STM) by our group [2], electrochemical scanning probe microscopy (SPM) including atomic force microscopy (AFM) has been widely used to study the surface film formation on graphite negative electrodes [2–15]. In almost all of these studies, highly oriented pyrolytic graphite (HOPG) has been used as a model graphite electrode [2–5,7–11,13,15]. The studies using HOPG have provided valuable information about

the surface film formation on graphite negative electrodes. On the other hand, composite graphite electrodes, which consist of graphite particles of several micrometers in size and a binder material, are used in commercially available lithium-ion batteries. Many types of graphite as well as carbon heat-treated at lower temperatures are used in commercially available batteries, and different kinds of graphite and carbon give different irreversible capacities, cycling efficiencies, and capacity retentions after storage. Thus, observation of the morphology changes of graphite or carbon particles in composite electrodes will be useful to understand subtle differences in surface film formation processes; however, only a few works using composite electrodes have been done so far [6,14]. This is mainly due to difficulties in observing composite electrodes by SPM because of their rough surfaces and gas evolution during charging.

In the present study, we used in situ AFM and investigated surface morphology changes of a composite graphite electrode in ethylene carbonate (EC)- and propylene carbonate (PC)-based solutions to show the applicability of SPM to studies on surface film formation on composite graphite electrodes.

* Corresponding author.

E-mail address: minaba@mail.doshisha.ac.jp (M. Inaba).

2. Experimental

Natural graphite powders (NG-3; nominal particle size, $5\ \mu\text{m}$) were kindly donated from The Kansai Coke and Chemicals Co., and used for preparation of composite graphite electrodes for in situ electrochemical AFM observation. The composite graphite electrodes were prepared from the graphite powder (NG-3), a carboxymethyl cellulose binder, and a styrene butadiene rubber binder in a weight ratio of 98:1:1 on a copper foil ($20\ \text{mm} \times 20\ \text{mm} \times 18\ \mu\text{m}$). AFM observation was carried out with an AFM system (PicoSPM[®], Molecular Imaging) equipped with a potentiostat (PicoStat[®], Molecular Imaging) and a laboratory-made electrochemical cell. The electrolyte solutions were

$1\ \text{mol dm}^{-3}$ (M) LiClO_4 dissolved in a 1:1 (v/v) mixture of EC + diethyl carbonate (DEC), and PC, which were purchased from Kishida Chemicals. The water content in each solution was less than 20 ppm. The counter and reference electrodes were lithium foil. Pyramidal silicon nitride tips were used for AFM measurements. AFM images in 1 M $\text{LiClO}_4/(\text{EC} + \text{DEC})$ were obtained repeatedly during constant current charging. In 1 M LiClO_4/PC , a potential step technique was used for AFM observation to avoid intensive exfoliation of the graphite electrode.

All measurements were carried out at $30\ ^\circ\text{C}$ in an argon-filled glovebox (Miwa, MDB-1B + MM3-P60S) with a dew point lower than $-60\ ^\circ\text{C}$. All potentials were referred to as volts versus Li^+/Li .

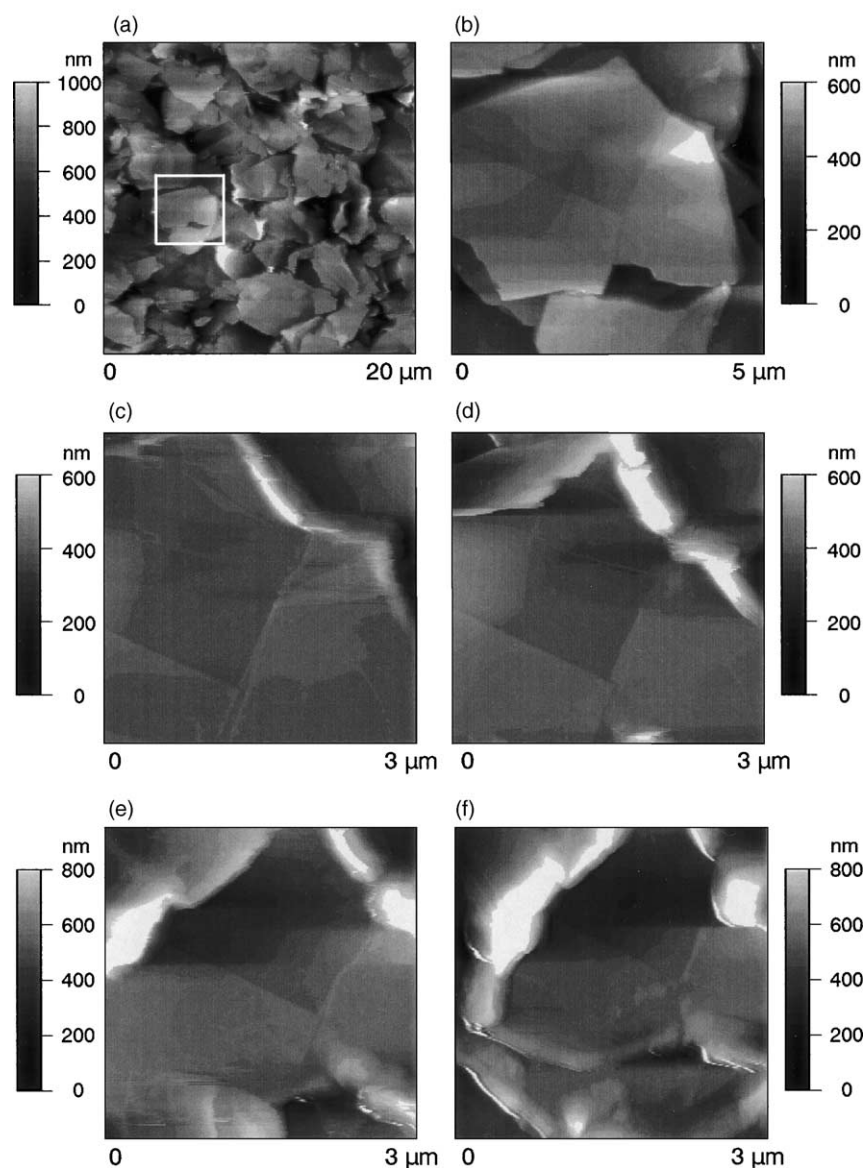


Fig. 1. AFM images of the composite graphite electrode surface obtained at the open circuit potential ($\sim 3.3\ \text{V}$) (a and b), $1.4\ \text{V}$ (c), $1.1\ \text{V}$ (d), $1.0\ \text{V}$ (e), and $0.8\ \text{V}$ during constant current charging at $30\ \mu\text{A cm}^{-2}$ in 1 M $\text{LiClO}_4/(\text{EC} + \text{DEC})$ (f). (a) $20\ \mu\text{m} \times 20\ \mu\text{m}$; (b) $5\ \mu\text{m} \times 5\ \mu\text{m}$; (c–f) $3\ \mu\text{m} \times 3\ \mu\text{m}$. The square in (a) shows the $5\ \mu\text{m} \times 5\ \mu\text{m}$ area in (b).

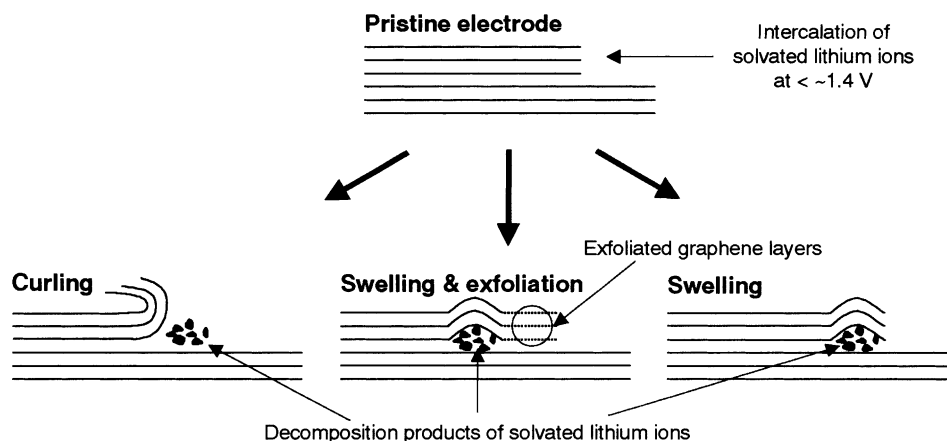


Fig. 2. Schematic models for the three topographical features observed in Fig. 1.

3. Results and discussion

3.1. Surface morphology changes in EC + DEC

Fig. 1 shows the surface morphology changes of the composite graphite electrode during constant current charging at $30 \mu\text{A cm}^{-2}$ in EC + DEC. Fig. 1a shows an AFM image ($20 \mu\text{m} \times 20 \mu\text{m}$) obtained at the open circuit potential ($\sim 3.3 \text{ V}$) before charging. The surface consists of

many graphite flakes of $6 \mu\text{m}$ or less in size. Fig. 1b shows a square area ($5 \mu\text{m} \times 5 \mu\text{m}$) in Fig. 1a. Several graphite flakes and their edges are clearly seen in this figure. AFM observation was focused on the surface morphology changes of a graphite flake located in the center of the image. During the charging, no topographical changes were observed at potentials more positive than 1.4 V . The surface morphology changes began at about 1.4 V (Fig. 1c). Part of the particle edge was slightly curled up. The curling of the edge

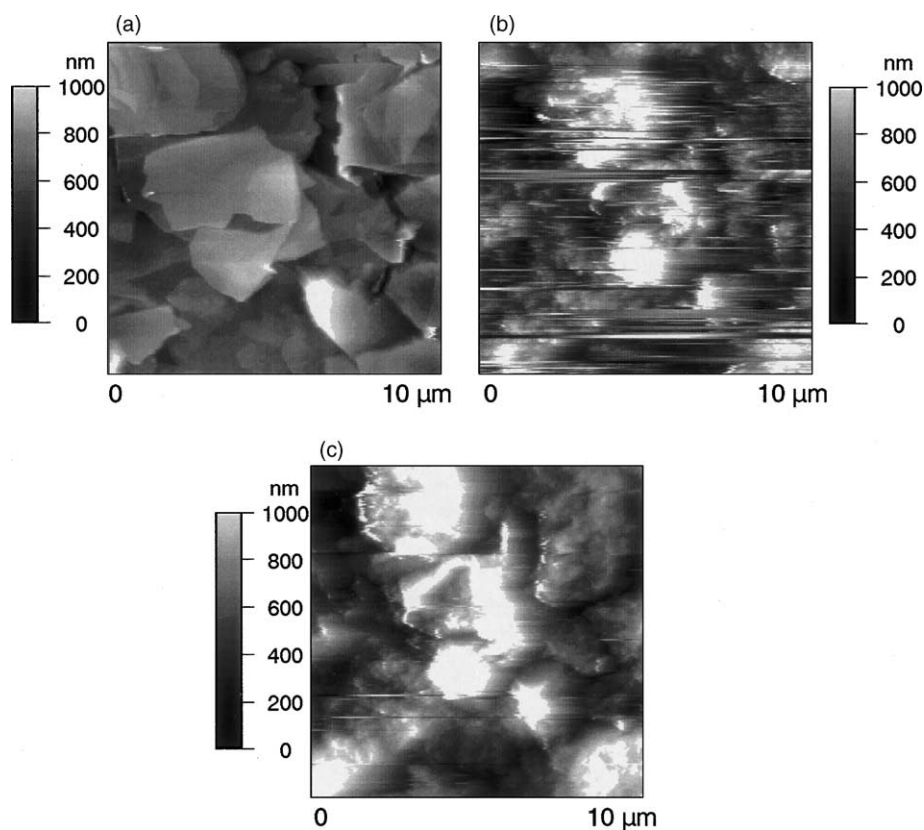


Fig. 3. AFM images ($10 \mu\text{m} \times 10 \mu\text{m}$) of the composite graphite electrode surface obtained before (a) and after charging to 0 V in $1 \text{ M LiClO}_4/(\text{EC} + \text{DEC})$ (b and c). Image (c) was obtained after repeated scanning.

proceeded further as the potential was lowered down to 0.8 V, as shown in Fig. 1c–e. Note that significant changes in contrast are seen, in particular, in the vicinity of the particle edge, with the lowering of the potential. These changes in contrast are not due to the effect of a potential change, but are attributed to real topographical changes of the surface, because we used AFM in the present study. The vicinity of the edge swelled and part of the edge exfoliated at 1.0 and 0.8 V, as shown in Fig. 1e and f. These three kinds of topographical changes (curling, swelling, and exfoliation) are schematically shown in Fig. 2. All these changes are attributable to the intercalation of a solvated lithium ion

(occurring at ~ 1.4 V) and their following decomposition between the graphene layers, on the basis of our previous results obtained for HOPG electrodes [2,3,11,13]. The results obtained for the composite graphite electrode are basically in good agreement with those obtained for HOPG electrodes; however, somewhat different features were observed as follows: (i) intercalation of a solvated lithium ion into the graphite particles began at a potential more positive than that into HOPG (~ 1.1 V); (ii) the curling of the edge was not observed on HOPG electrodes; and (iii) the formation of hill-like structures and their growth into the interior was not observed on graphite particles; instead,

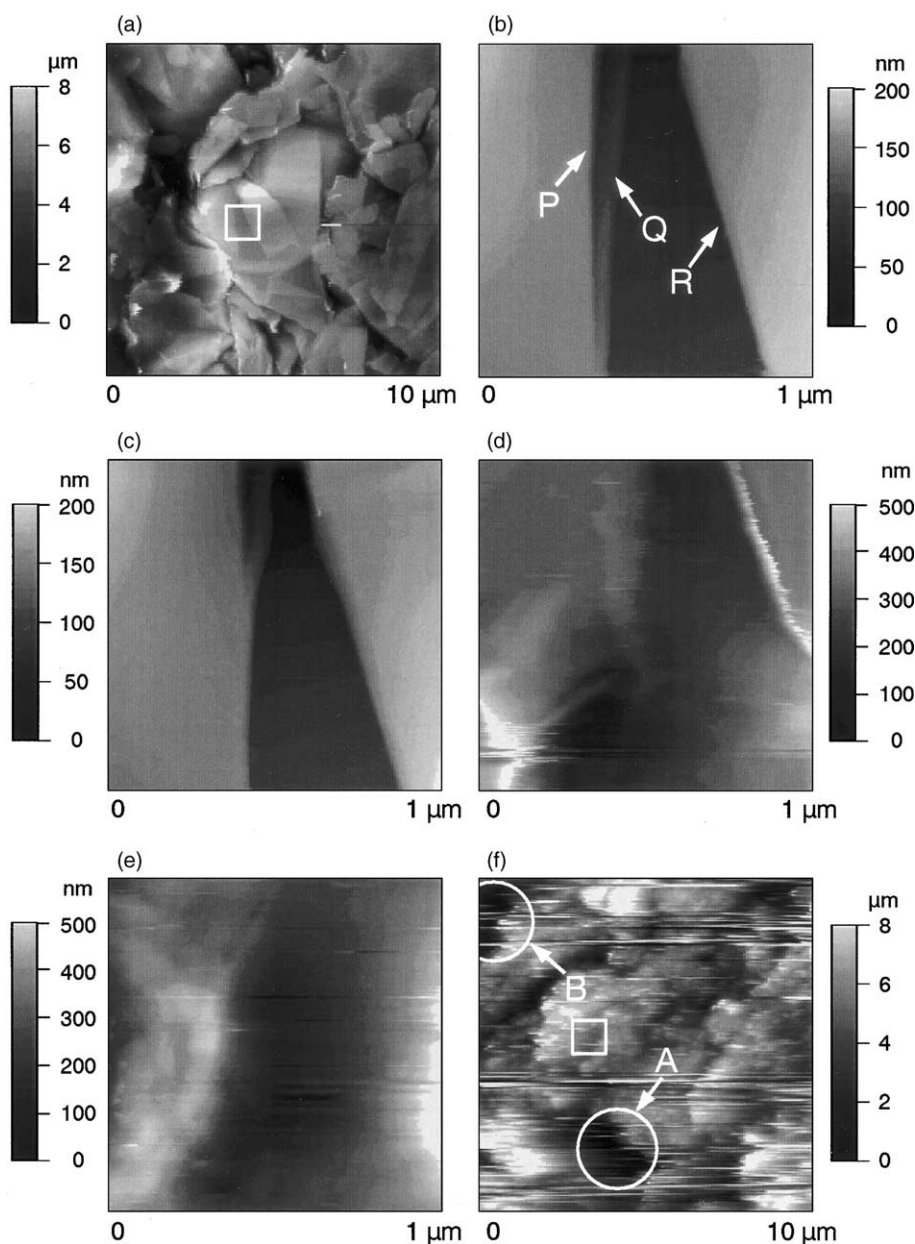


Fig. 4. AFM images of the surface of the composite graphite electrode obtained at 3.0 V before (a) and after potential step experiments (b–f). The potential was stepped to 1.0 V for 3 min (b); and to 0.9 V for 3 min (c), 30 min (d), and 60 min in 1 M LiClO₄/PC (e and f). (a and f) 10 μm × 10 μm; (b–e) 1 μm × 1 μm. The squares in (a and f) show the 1 μm × 1 μm area in (b–e).

the swelling along the edge appeared. Although the details are not clear at present, one plausible reason is a difference in the edge plane structure between HOPG and graphite particles, because the solvent co-intercalation reaction is greatly affected by the host structure [16,17].

Fig. 3 shows AFM images of nearly the same area of $10\ \mu\text{m} \times 10\ \mu\text{m}$ obtained before and after charging. After charging, the whole surface of the composite graphite electrode was covered with precipitates, as shown in Fig. 3b. The precipitates are considered to be direct decomposition products of the electrolyte solution on the basal and edge planes of graphite particles. In previous studies, we reported that the precipitates can be scraped off by repeated AFM scanning with the microcantilever in the contact mode [11,13]. An AFM image after repeated scanning is shown in Fig. 3c. Although the precipitates could not be removed completely, the morphologies of the other graphite flakes were also significantly changed after the charging. This confirms that solvent co-intercalation occurred at every graphite flake.

3.2. Surface morphology changes in PC

Fig. 4 shows the surface morphology changes of the composite graphite electrode before and after potential steps in PC. Fig. 4a shows an AFM image ($10\ \mu\text{m} \times 10\ \mu\text{m}$) obtained at 3.0 V before potential step experiments. The surface was stable for several hours, which confirmed that the electrode surface is quite inert and neither deposition nor intercalation reaction takes place at 3.0 V. The surface morphology of a $1\ \mu\text{m} \times 1\ \mu\text{m}$ area indicated by a square in Fig. 4a was monitored after potential steps.

The potential was successively lowered by 100 mV from 3.0 V. No morphology changes were observed at potentials more positive than 0.9 V. A typical image in this potential range is shown in Fig. 4b, which was obtained after a potential step to 1.0 V for 3 min. Three step edges designated as P, Q, and R on a graphite flake were clearly observed in this figure. After the potential was stepped to 0.9 V for 3 min (Fig. 4c), part of step Q disappeared, indicating that this part of graphite layers exfoliated by the intercalation of a solvated lithium ion, but the swellings that appeared in the EC + DEC solution was not observed. The exfoliation proceeded further as the holding time at 0.9 V was elongated, as shown in Fig. 4d and e. Step Q completely disappeared after a potential step to 0.9 V for 30 min (Fig. 4d), and the original step-and-terrace structure was ruptured significantly after another potential step to 0.9 V for 60 min (Fig. 4e). It is clear that intensive solvent co-intercalation occurred at all step edges.

Fig. 4f shows an expanded area of $10\ \mu\text{m} \times 10\ \mu\text{m}$. The $1\ \mu\text{m} \times 1\ \mu\text{m}$ area in Fig. 4e is indicated by a square in Fig. 4f. Dramatic changes in surface morphology are seen in Fig. 4f. The shape of each graphite flake seen in Fig. 4a significantly changed after the potential steps to 0.9 V. This is due to the exfoliation of graphite layers that was caused by solvent co-intercalation in the PC solution. Another dis-

tinctive feature seen in Fig. 4f is the formation of holes indicated by circles, which were not seen in the original image (Fig. 4a). When a composite graphite electrode is charged in PC, its potential dropped rapidly and remained nearly constant at $\sim 0.9\ \text{V}$ [16]. Furthermore, it was reported that propylene gas is produced from a graphite electrode when it is polarized at negative potentials in PC solutions [18,19]. Therefore, it is reasonable to consider that vigorous propylene gas evolution from the inside of the composite graphite electrode is responsible for the formation of the holes.

4. Conclusions

Surface film formation on a composite graphite negative electrode, which is similar to that used in commercially available lithium-ion batteries, was investigated by in situ AFM. At the initial stage of charging (between 0.8 and 1.4 V) in EC + DEC, solvated lithium ion was intercalated into graphite particles in the composite electrode and then the solvent molecules decomposed between the graphene layers, which caused three types of morphological changes of the particles: curling, swelling, and exfoliation. These results supported the mechanism for the surface film formation obtained using HOPG as a model graphite electrode. In PC, co-intercalation of the solvent molecules occurred intensively, and caused vigorous exfoliation and rupturing of graphene layers of the particles, which is also in agreement with the results obtained for HOPG. In addition, a deterioration by the formation of holes in the composite graphite electrode was observed in PC, which was attributed to gas evolution upon decomposition of PC molecules. The results obtained in the present study clearly indicated that AFM can be conveniently used for observation of the surface morphology changes of composite graphite electrodes. This technique is expected to be applied to composite electrodes employing various kinds of graphite or carbon.

Acknowledgements

The authors thank The Kansai Coke and Chemicals Co., for donating the graphite powders (NG-3). This work was supported by CREST of Japan Science and Technology (JST).

References

- [1] Z. Ogumi, M. Inaba, Bull. Chem. Soc. Jpn. 71 (1998) 521.
- [2] M. Inaba, Z. Siroma, A. Funabiki, Z. Ogumi, T. Abe, Y. Mizutani, M. Asano, Langmuir 12 (1996) 1535.
- [3] M. Inaba, Z. Siroma, Y. Kawatate, A. Funabiki, Z. Ogumi, J. Power Sources 68 (1997) 221.
- [4] K.A. Hirasawa, T. Sato, H. Asahina, S. Yamaguchi, S. Mori, J. Electrochem. Soc. 144 (1997) L81.

- [5] C. Chu, J.Y. Josefovicz, G.C. Farrington, J. Electrochem. Soc. 144 (1997) 4161.
- [6] K. Morigaki, T. Fujii, A. Ohta, *Denki Kagaku (Electrochemistry)* 66 (1998) 1114.
- [7] M. Inaba, Y. Kawatate, A. Funabiki, S.-K. Jeong, T. Abe, Z. Ogumi, *Electrochim. Acta* 45 (1999) 99.
- [8] M. Inaba, Y. Kawatate, A. Funabiki, S.-K. Jeong, T. Abe, Z. Ogumi, *Electrochemistry* 67 (1999) 1153.
- [9] Z. Ogumi, S.-K. Jeong, M. Inaba, T. Abe, *Macromol. Symp.* 156 (2000) 195.
- [10] D. Allita, R. Kotz, P. Novak, H. Siegenthaler, *Electrochem. Commun.* 2 (2000) 436.
- [11] S.-K. Jeong, M. Inaba, T. Abe, Z. Ogumi, *J. Electrochem. Soc.* 148 (2001) A989.
- [12] F. Kong, R. Kostecki, G. Nadeau, X. Song, K. Zaghbi, K. Kinoshita, F. McLarnon, *J. Power Sources* 97–98 (2001) 56.
- [13] S.-K. Jeong, M. Inaba, R. Mogi, Y. Iriyama, T. Abe, Z. Ogumi, *Langmuir* 17 (2001) 8281.
- [14] M. Koltypin, Y.S. Cohen, B. Markovsky, Y. Cohen, D. Aurbach, *Electrochem. Commun.* 4 (2002) 17.
- [15] S.-K. Jeong, M. Inaba, R. Mogi, Y. Iriyama, T. Abe, Z. Ogumi, *Electrochim. Acta* 47 (2002) 1975.
- [16] T. Abe, Y. Mizutani, T. Tabuchi, K. Ikeda, M. Asano, T. Harada, M. Inaba, Z. Ogumi, *J. Power Sources* 68 (1997) 216.
- [17] K. Guerin, A. Fevrier-Bouvier, S. Flandrois, M. Couzi, B. Simon, P. Biensan, *J. Electrochem. Soc.* 146 (1999) 3660.
- [18] A.N. Dey, B.P. Sullivan, *J. Electrochem. Soc.* 117 (1970) 222.
- [19] G. Eichinger, *J. Electroanal. Chem.* 74 (1976) 183.