

Preparation of surface-modified carbonaceous thin-film electrodes by NF_3 plasma and their electrochemical properties

Tomokazu Fukutsuka^{a,*}, Satoshi Hasegawa^a, Yoshiaki Matsuo^a, Yosohiro Sugie^a, Takeshi Abe^b, Zempachi Ogumi^b

^a Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2201, Japan

^b Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

Available online 27 April 2005

Abstract

Carbonaceous thin-film electrodes were modified by nitrogen trifluoride (NF_3) plasma, and surface-modified carbonaceous thin-film electrodes were obtained and investigated by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and Auger electron spectroscopy (AES). Their chemical composition, degree of fluorination, and chemical bonding were investigated. The effects of surface modification on the anode reaction of lithium-ion batteries were examined. The electrochemical properties of the resultant thin-film electrodes were investigated by cyclic voltammetry using a three-electrode electrochemical cell. The cyclic voltammograms showed that the fluorine atoms on the surface suppressed the reductive decomposition of ethylene carbonate.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Carbon; Lithium-ion batteries; Solid electrolyte interface; Surface modification; Thin-film electrode

1. Introduction

For the recent development of mobile devices, lithium-ion batteries have been extensively studied because of their high performance and potentialities [1,2]. The further improvement of energy density will require a reduction in the irreversible capacity of lithium-ion batteries. The formation of a surface film, which is called the solid electrolyte interface (SEI), on the carbon negative electrode is a main cause of irreversible capacity. Since SEI is derived from reductive decomposition of the electrolyte solution, reductive decomposition of the electrolyte should be minimized to improve the energy density of lithium-ion batteries. It has been reported that SEI is composed of inorganic compounds, such as LiF , Li_2CO_3 , etc., organic compounds, such as lithium alkyl carbonate and lithium alkoxides, and polymer-like substances with repeating oxyethylene units [3–5]. If fluorine atoms or oxygen atoms exist on the surface of carbon, it is expected

that these heteroatoms will react with the electrolyte and salt electrochemically or chemically, and these atoms act as a precursor of SEI. Therefore, the introduction of heteroatoms to the surface of carbon is quite useful. Various surface modifications of the carbon negative electrode have been studied. Peled et al. reported that mild oxidation of graphite introduced oxygen atoms to the graphite, and these oxygen atoms then react with electrolyte solution and act as chemically bonded SEI (CB-SEI) [6]. Nakajima et al. reported that the irreversible capacity of surface-fluorinated petroleum cokes is decreased because of the LiF formed by the reduction of fluorine atom [7].

We have prepared carbonaceous thin-film electrodes by plasma-assisted chemical vapor deposition (plasma CVD), and such electrodes are suitable for the study of surface properties [8–16]. Previously, we reported that the side reaction in the first reduction process was suppressed by surface plasma modification in the reduction of the electrolyte solution at the first cycle [10,14]. With the use of plasma, mild surface modification can be achieved without changing the bulk electrochemical properties. In this paper, we report

* Corresponding author. Tel.: +81 792 67 4948; fax: +81 792 67 4948.
E-mail address: fuku@eng.u-hyogo.ac.jp (T. Fukutsuka).

surface-modified carbonaceous thin-film electrodes obtained by using NF_3 plasma and their effects on the electrochemical properties of the thin films as negative electrodes of lithium-ion batteries.

2. Experimental

Carbonaceous thin-film electrodes were prepared on nickel sheets by plasma CVD from acetylene and argon. Substrates were placed on a ground electrode maintained at 873 K. The applied rf power was set to 50 W and the resulting thin films were less than 1.0 μm thick. The details have been described previously [8,12]. The same apparatus was used for surface plasma modification of the obtained thin-film electrodes. The reaction gases were NF_3 (Kanto Denka Kogyo Co. Ltd.) and argon, and the temperature of the thin films was maintained below 373 K. The flow rate of NF_3 was set at 5–20 sccm. The applied rf power was set at 50 W and the treatment time was 5 min.

The surface crystallinity of carbonaceous thin-film electrodes was characterized by Raman spectroscopy (Jobin-Yvon, T64000). X-ray photoelectron spectroscopy (XPS) with Mg $K\alpha$ line radiation (JEOL, JAMP7800F) was used for surface chemical analysis. Auger electron spectroscopy (AES) was also used for local elemental analysis (JEOL, JAMP7800F).

A three-electrode electrochemical cell was used for electrochemical measurements. Carbonaceous thin-film electrode was used as a working electrode and lithium metal was used as both counter and reference electrodes. Electrolyte solutions were a mixture (1:1 by volume) of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1 mol dm^{-3} LiClO_4 (Kishida Kagaku), EC containing 1 mol dm^{-3} LiClO_4 (Kishida Kagaku), and DEC containing 1 mol dm^{-3} LiClO_4 (Kishida Kagaku). Vinylene carbonate (VC; Aldrich) was used as an additive (5 vol%) for EC solution. The cell was assembled in an argon-filled glove box. Electrochemical properties were studied by cyclic voltammetry (RADIOMETER, VoltaLab 21) with a sweep rate of 1 mV s^{-1} in the potential range of 3–0 V. Unless otherwise stated, the potential is referenced to Li/Li^+

3. Results and discussion

The surface of the carbonaceous thin-film electrodes prepared by plasma CVD was very flat and contained no pinholes within the range of the SEM image [12]. The Raman spectra of the carbonaceous thin-film electrodes modified by NF_3 plasma with an applied rf power of 50 W are shown in Fig. 1. Three main peaks were observed at around 1360, 1580, and 1620 cm^{-1} . The peak at around 1580 cm^{-1} is assigned to the Raman active E_{2g} mode frequency (G band) [17]. The peak at around 1360 cm^{-1} is the Raman inactive A_{1g} mode frequency [17]. The peaks at around 1360 and 1620 cm^{-1} appear in the

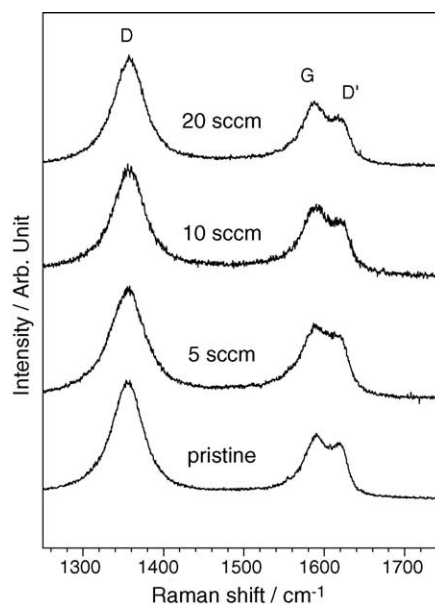


Fig. 1. Raman spectra of carbonaceous thin-film electrodes modified by NF_3 plasma at an rf power of 50 W for 5 min. Flow rates of NF_3 : 5, 10, and 20 sccm.

case of finite crystal size and imperfection of carbonaceous materials [18]; the former is called the D band and the latter is the D' band. In these Raman spectra, obvious changes were not noted on plasma modification, indicating that the fluorine radicals in the present plasma modification caused little damage to carbonaceous thin-film electrodes. Thus, the crystallinity of the surface of carbonaceous thin-film electrodes was not changed after plasma modification.

XPS measurements were carried out to estimate the surface condition of the fluorination of carbonaceous thin-film electrodes. Fig. 2 shows XPS C 1s spectra of carbonaceous thin-film electrodes modified by NF_3 plasma with various flow rates. In Fig. 2(a), only one peak appeared at 284 eV for the C 1s spectrum. This peak is assigned to C–C bonding (graphite). Further, no peak was observed for the F 1s spectrum. In Fig. 2(b), two peaks are seen in the C 1s spectrum at around 284 and 288 eV for thin-film electrodes modified by NF_3 plasma at 20 sccm. The former is assigned to C–C bonding, and the latter has been reported to be nearly semi-ionic or semi-covalent C–F bonding observed in fluorinated stage 1 fluorine–graphite intercalation compounds [19]. Furthermore, for the F 1s spectra, only one peak appeared at 687 eV; this peak corresponded to semi-ionically bonded fluorine atoms, as mentioned above. From these results, it is obvious that carbonaceous thin-film electrodes were fluorinated by NF_3 plasma modification, and fluorine atoms on the carbonaceous thin-film electrodes are semi-ionically bonded to carbon atoms. From XPS measurements, the F/C values were calculated as follows: 0.143 (modified by 5 sccm), 0.135 (modified by 10 sccm), and 0.142 (modified by 20 sccm). Since the atomic ratio obtained from XPS measurement is affected by the chemical composition of the bulk region, the F/C values are not sufficient to estimate surface properties.

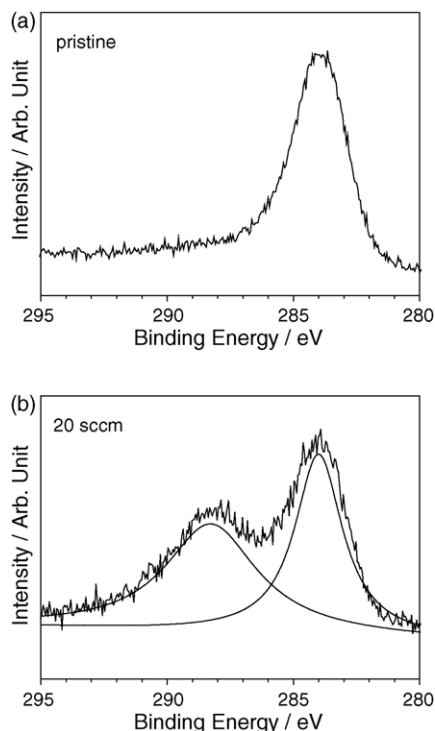


Fig. 2. C 1s XPS spectra of carbonaceous thin-film electrodes modified by NF_3 plasma. Flow rates of NF_3 : (a) pristine and (b) 20 sccm.

AES was used to evaluate the degree of surface fluorination, since AES measurement is very sensitive to the surface region. The F/C values were calculated from the peak intensity of the derivative Auger spectra (peak-to-peak method) and the results were as follows: 0.495 (modified by 5 sccm), 0.535 (modified by 10 sccm), and 0.545 (modified by 20 sccm). From this result, the F/C value increased with an increase in the flow rate of NF_3 . Moreover, these values are larger than those obtained from XPS, which indicates that the fluorination of carbonaceous thin-film electrodes took place predominantly in the surface region. The values of F/C are in the range of 0.495–0.545, which corresponds to that of C_2F . This composition is close to that of the semi-ionic stage 1 fluorine–graphite intercalation compound [19], and this result is in good agreement with the result of XPS measurement. From the above results, it is clear that an increase in the flow rate of NF_3 leads to an increase in the degree of fluorination.

The immersion potential of the pristine thin-film electrode was about 3.2 V, and the immersion potentials of plasma-modified thin-film electrodes ranged between 3.8 and 4.2 V. These values suggest that the surface of carbonaceous thin-film electrodes is changed by NF_3 plasma, i.e., the surface of the thin-film electrodes is fluorinated, which is in good agreement with the results of XPS and AES measurements. Fig. 3 shows the cyclic voltammograms (CVs) of the first cycle for carbonaceous thin-film electrodes. For the pristine thin-film electrode (Fig. 3(a)), a small peak appears at about

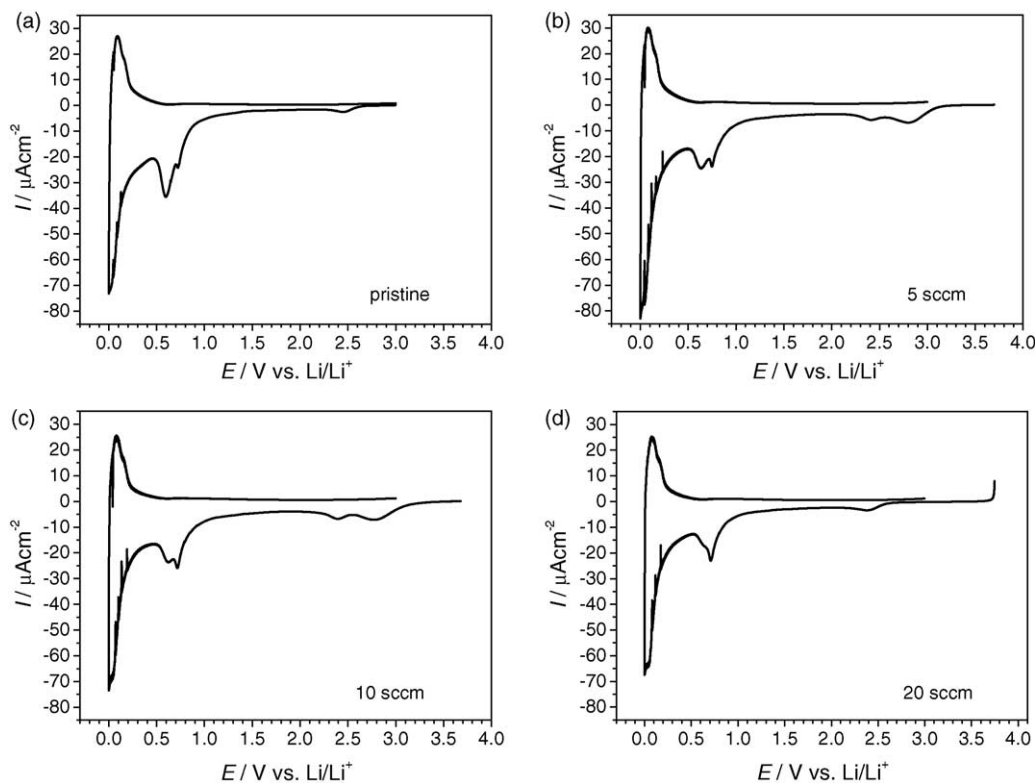


Fig. 3. Cyclic voltammograms (first cycle) of carbonaceous thin-film electrodes modified by NF_3 plasma. Electrolyte: $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC} + \text{DEC}$ (1:1), sweep rate: 1 mV s^{-1} . Flow rates of NF_3 : (a) pristine, (b) 5 sccm, (c) 10 sccm, and (d) 20 sccm.

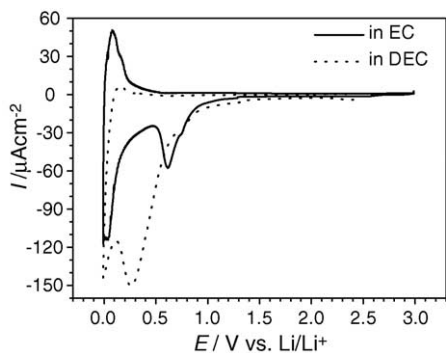


Fig. 4. Cyclic voltammograms of pristine carbonaceous thin-film electrodes. Sweep rate: 1 mV s^{-1} . Electrolytes are $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC}$ (solid line) and $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{DEC}$ (dotted line).

0.8 V and a large peak appears at about 0.6 V in the reduction process. These peaks suggest the reductive decomposition of solvent and the formation of a solid electrolyte interface on the surface of carbonaceous thin-film electrodes. Obvious changes were observed in CVs of plasma-modified thin-film electrodes. In the CV of a carbonaceous thin-film electrode modified at 5 sccm (Fig. 3(b)), the reduction peak at about 0.6 V was drastically decreased compared with that of the pristine thin-film electrode. This tendency became more pronounced with an increase in the flow rate of NF_3 , and the peak

at about 0.6 V almost disappeared for the thin-film electrode modified at 20 sccm (Fig. 3(d)). There was no difference between the first-cycle CVs and the second-cycle CVs for all the thin-film electrodes. Therefore, the surface fluorination of carbonaceous thin-film electrodes only affects the first cycle of CV. These results suggest that it is concluded that the surface fluorination of carbonaceous thin films suppresses the reductive reaction of solvent that occurs at about 0.6 V while retaining the bulk electrochemical properties.

Next, CVs were measured in electrolyte solutions containing a single solvent of EC or DEC to elucidate which solvent (EC or DEC) reacts at about 0.6 V. Fig. 4 shows the CVs of pristine thin-film electrodes in EC and DEC for the first cycle. CVs indicate that the reductive decomposition of EC and DEC occurs mainly at about 0.6 and 0.3 V, respectively. From these results, the reduction peak at about 0.6 V can be assigned to the reductive decomposition of EC, and the surface fluorination of carbonaceous thin-film electrodes by NF_3 plasma suppressed the reductive reaction of EC at the first Li^+ insertion process. Previously, we reported that the reductive reaction of EC at about 0.6 V was associated with the formation of SEI by using VC and ethylene sulfite (ES) as additives in an EC + DEC solution [14]. Therefore, fluorine atoms on carbonaceous thin-film electrodes gave C–F bonding, and the reaction products formed by the chemical or electrochemical reaction between these bonds and solvent acted as a passi-

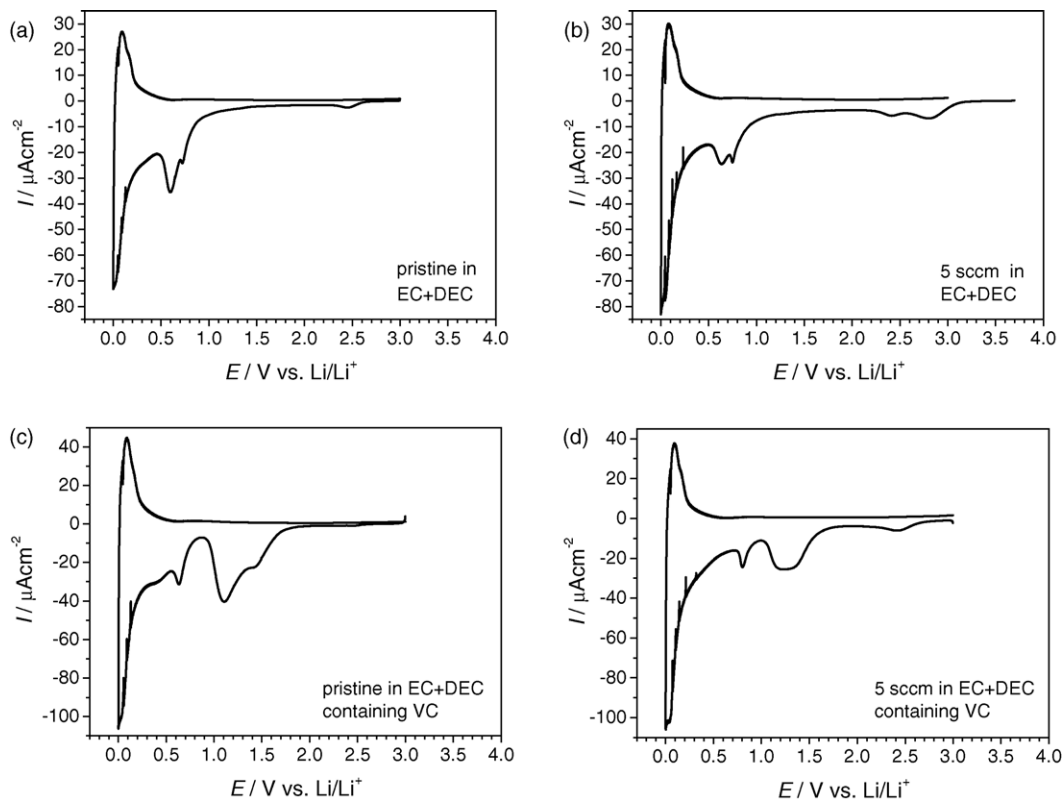


Fig. 5. Cyclic voltammograms (first cycle) of pristine carbonaceous thin-film electrodes (a and c) and surface-modified (NF_3 ; 5sccm) carbonaceous thin-film electrodes (b and d). Electrolyte: $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC} + \text{DEC}$ (1:1) (a and b) and $1 \text{ mol dm}^{-3} \text{ LiClO}_4/\text{EC} + \text{DEC}$ (1:1) containing VC (5 vol%) (c and d). Sweep rate: 1 mV s^{-1} .

vation film, leading to the suppression of further reductive reaction at about 0.6 V to form SEI.

Finally, the combination of surface modification and the use of VC was carried out to more effectively suppress the reductive decomposition of EC. Fig. 5 shows CVs (first cycle) of pristine thin-film electrodes and plasma-modified thin-film electrodes by 5 sccm in EC + DEC solution without and with VC. For Fig. 5(b and c), the reductive reaction of EC was suppressed by surface fluorination and the addition of VC to EC + DEC. However, their effects were insufficient to completely suppress the reductive reaction of EC. Next, CV of plasma-modified thin-film electrodes by 5 sccm was obtained in EC + DEC containing VC (Fig. 5(d)). There was almost no reductive current due to the reductive reaction of EC at 0.6 V compared with the CV for a pristine thin-film electrode in EC + DEC (Fig. 5(a)). Thus, these two effects completely suppressed the reductive reaction of EC. The following mechanism can be proposed based on the above results: VC is reduced at a more noble potential than the reduction potential of EC, and the decomposition products form organic compounds. On the other hand, C–F bonds react with electrolyte and form inorganic compounds. These two kinds of compounds act as a passivating film and suppress the further reductive reaction of EC at about 0.6 V. This result indicates that inorganic compounds introduced by surface modification as well as organic compounds are quite useful for suppressing the reductive reaction of the main solvent.

4. Conclusion

Surface-modified carbonaceous thin-film electrodes were prepared by using NF_3 plasma, and their surfaces were fluorinated. XPS and AES measurements revealed that fluorination took place predominantly in the surface region and the degree of fluorination was dependent on the flow rate of NF_3 and introduced C–F bonding is semi-ionic bonding. Cyclic

voltammograms indicated that the reductive reaction of EC at the first reduction process was suppressed by fluorination. These results suggest that surface modification of carbonaceous thin-film electrodes by NF_3 plasma is very effective for decreasing the reductive reaction of the electrolyte in lithium-ion batteries.

References

- [1] Z. Ogumi, M. Inaba, Bull. Chem. Soc. Jpn. 71 (1998) 521.
- [2] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novák, Adv. Mater. 10 (1998) 725.
- [3] D. Bar-Tow, E. Peled, L. Burstein, J. Electrochem. Soc. 146 (2001) 824.
- [4] D. Aurbach, Y. Ein-Eli, O. Chusid (Youngman), Y. Carmeli, M. Babai, H. Yamin, J. Electrochem. Soc. 141 (1994) 603.
- [5] Z. Ogumi, A. Sano, M. Inaba, T. Abe, J. Power Sources 97–98 (2001) 156.
- [6] E. Peled, C. Menachem, D. Bar-Tow, A. Melman, J. Electrochem. Soc. 143 (1996) L4.
- [7] T. Nakajima, J. Li, K. Naga, K. Yoneshima, T. Nakai, Y. Ohzawa, J. Power Sources 133 (2004) 243.
- [8] T. Abe, T. Fukutsuka, M. Inaba, Z. Ogumi, Carbon 37 (1999) 1165.
- [9] T. Fukutsuka, T. Abe, M. Inaba, Z. Ogumi, N. Tsuji, A. Tasaka, Tanso 190 (1999) 252.
- [10] T. Fukutsuka, T. Abe, M. Inaba, Z. Ogumi, Mol. Cryst. Liq. Cryst. 340 (2000) 517.
- [11] T. Fukutsuka, T. Abe, M. Inaba, Z. Ogumi, Y. Matsuo, Y. Sugie, Carbon Sci. 1 (2001) 129.
- [12] T. Fukutsuka, T. Abe, M. Inaba, Z. Ogumi, J. Electrochem. Soc. 148 (2001) A1260.
- [13] T. Fukutsuka, Y. Matsuo, Y. Sugie, T. Abe, M. Inaba, Z. Ogumi, Mol. Cryst. Liq. Cryst. 388 (2002) 117.
- [14] T. Fukutsuka, S. Hasegawa, T. Katayama, Y. Matsuo, Y. Sugie, T. Abe, Z. Ogumi, Electrochemistry 71 (2003) 1111.
- [15] T. Abe, T. Fukutsuka, S. Yamate, Y. Iriyama, M. Inaba, Z. Ogumi, Mol. Cryst. Liq. Cryst. 388 (2002) 141.
- [16] Z. Ogumi, T. Abe, T. Fukutsuka, S. Yamate, Y. Iriyama, J. Power Sources 127 (2004) 72.
- [17] F. Tuinstra, J.L. Koenig, J. Chem. Phys. 53 (1970) 1126.
- [18] G. Katagiri, Tanso 175 (1996) 304 (in Japanese).
- [19] Y. Matsuo, T. Nakajima, Z. Anorg. Allg. Chem. 621 (1995) 1943–1950.