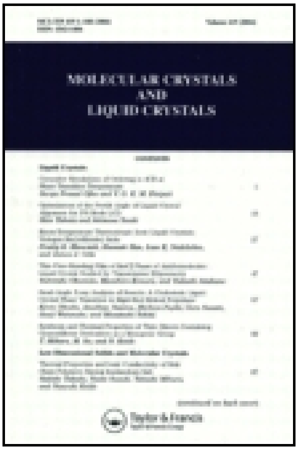

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Surface Modification Of Carbonaceous Thin Films By Nf 3 Plasma And Their Effects On Electrochemical Properties

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SURFACE MODIFICATION OF CARBONACEOUS THIN FILMS BY NF_3 PLASMA AND THEIR EFFECTS ON ELECTROCHEMICAL PROPERTIES

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Carbonaceous thin films were prepared by plasma-assisted chemical vapor deposition. Surface of resultant films were treated by NF_3 plasma at room temperature. From Raman spectra, crystallinity of sample remained almost unchanged by the surface treatment. The reduction current at 0.6 V vs. Li/Li^+ in the cyclic voltammograms at the 1st cycle decreased with increasing the flow rate of NF_3. This result indicates that fluorine atoms bonded to carbon atoms play an important role in decreasing the side reaction at the 1st reduction process.

Keywords: carbonaceous thin film; surface modification; lithium ion battery

INTRODUCTION

For the recent development of mobile devices, lithium ion batteries have been extensively studied because of their high performance and potentialities [1]. In regard to the negative electrode, highly crystallized graphite has been used in commercial market because intercalation/de-intercalation of lithium ion proceeds in graphite at the potential as low as redox potential of lithium metal [2]. However, carbonaceous materials have been still extensively investigated as negative electrode materials to improve the performance of lithium ion batteries [3–10].

At the first charge of lithium ion batteries, it is well known that reduction of electrolyte on the negative electrode occurs and that passivation

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film (solid electrolyte interface: SEI) is formed around 1.0 V vs. Li/Li^+ [1,2]. Although the formation of SEI results in the large part of irreversible capacity, the SEI is essential for suppression of the further decomposition of electrolyte, leading to almost 100% cycle efficiency.

Various surface modifications on graphite electrodes have been applied for the effective formation of SEI [11–13]. We have reported the synthesis of sp^2-type carbonaceous thin films by plasma-assisted chemical vapor deposition (plasma CVD) and studied their electrochemical properties as the binder free negative electrodes [14–18]. Homogeneous surface modification of the films is quite easy, because of the film's flatness and smoothness. Therefore, the effect of surface modification of carbonaceous materials on electrochemical properties can be clearly elucidated.

In this paper, we report surface modification of carbonaceous thin films by nitrogen trifluoride (NF_3) plasma and their effects on structures and electrochemical properties of the films as negative electrodes for lithium ion batteries.

EXPERIMENTAL

Carbonaceous thin films were deposited on substrates of nickel sheets from acetylene and argon. Substrates were placed on a ground electrode keeping at 873 K. The applied RF power was set to 50 W. The detail procedure was shown in our previous paper [14,18].

The same apparatus was used for surface plasma modification of the films. NF_3 (Kanto Denka Kogyo Co., Ltd.) was used as fluorine sources and argon was plasma assist gas, and the temperature of films was kept below 373 K. The flow rate of NF_3 was set at 5, 10 and 20 sccm. Applied RF power was chosen to be 50 W, and the treatment time was 5 min. The use of NF_3 for surface treatment makes it possible to fluorinate carbonaceous thin films without heating, because NF_3 can release fluorine radicals in plasma, and the polymerization compound is not formed because of the absence of carbon atom in NF_3.

Resultant films were characterized by Raman spectroscopy (Jobin-Yvon, T64000) with 514.5 nm line of an argon ion laser. X-ray photoelectron spectroscopy (XPS) was used for surface chemical analysis of the films (JEOL, JUMP7800F). Auger electron spectroscopy (AES) with field emission type electron gun (JEOL, JUMP7800F) was used for the local elemental analysis of the films.

A three-electrode electrochemical cell was employed for electrochemical measurements. Lithium metal was used as counter and reference electrodes. The electrolyte solution was a mixture (1:1 by volume) of ethylene carbonate (EC) and diethyl carbonate (DEC) containing 1 mol dm^{-3} $LiClO_4$

(TOMIYAMA PURE CHEMICAL INDUSTRIES, LTD). 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 in the potential range of 3 to 0 V vs. Li/Li^+.

RESULTS AND DISCUSSION

The surface of carbonaceous thin film prepared by plasma CVD was apparently flat and no pin-hole was observed within the SEM image [18]. The Raman spectra of carbonaceous thin films treated by NF_3 plasma are shown in Figure 1. In these Raman spectra, obvious change by plasma treatment was not recognized.

From XPS spectra for pristine film, only one peak appeared at 284 eV for C1s spectrum. This peak is assigned to C-C bonding (graphite). No peak was observed for F1s spectrum. XPS spectra for treated films gave two peaks in C1s spectrum at around 284 eV and 288 eV. The former is assigned to C-C bonding and the latter is reported as semi-ionic or semi-covalent C-F bonding observed in stage 1 fluorine-graphite intercalation compounds, C_2F-$C_{2.5}F$ [19]. And for all F1s spectra, only one peak appeared at 687 eV, corresponding to semi-ionically bonded fluorine atoms. From these results, carbonaceous thin films were fluorinated by NF_3 plasma treatment, and fluorine atoms on the carbonaceous thin films are semi-ionically bonded to carbon atoms. AES was used for the evaluation of degree of fluorination by the change of flow rate of NF_3. Table 1 shows the atomic ratio of fluorine atom to carbon atom (F/C) of films evaluated from the peak intensity of

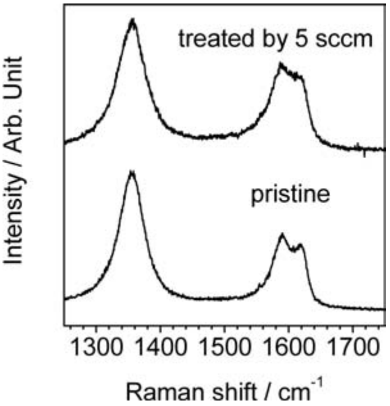

FIGURE 1 Raman spectra of carbonaceous thin films treated by NF_3 plasma at RF power of 50 W for 5 min. Flow rates of NF_3: 5 sccm.

TABLE 1 The F/C Values Evaluated from AES Spectra

Flow rate of NF_3	Atomic rate (F/C)
5 sccm	0.495
10 sccm	0.535
20 sccm	0.545

derivative Auger spectra (peak to peak method). The F/C value increased with increase of the flow rate of NF_3. The values of F/C are in the range of 0.495 to 0.545, and therefore the composition of treated films is close to C_2F, the semi-ionic stage 1 fluorine-graphite intercalation compound C_2F [19]. From the above results, it is clear that increment of flow rate of NF_3 lead to the increment of the degree of fluorination.

In Figure 2, cyclic voltammograms (CVs) of the 1st and 2nd cycles for carbonaceous thin films are shown. For pristine film (Fig. 2a), small peak at about 0.8 V and large peak at about 0.6 V appear in the 1st reduction process. These peaks suggest the decomposition of solvent, and the decomposition products act as SEI on the surface of carbonaceous thin films [1,2]. Obvious change was observed for the CVs of plasma treated films. For the CV of carbonaceous thin film treated at 5 sccm (Fig. 2b), the reduction peak about 0.6 V drastically decreased as compared with that for pristine film. The reduction peak became small by increasing the flow rates of NF_3, and the peak at 0.6 V almost disappeared for the film treated by 20 sccm. In addition, the shapes of cyclic voltammograms of the 2nd cycle for surface treated films are very similar with that of the 2nd cycle for pristine film. Therefore, surface fluorination of carbonaceous thin films only affects on the 1st cycle of CV. Open circuit potential (OCP) of treated films (ca 3.8 V)

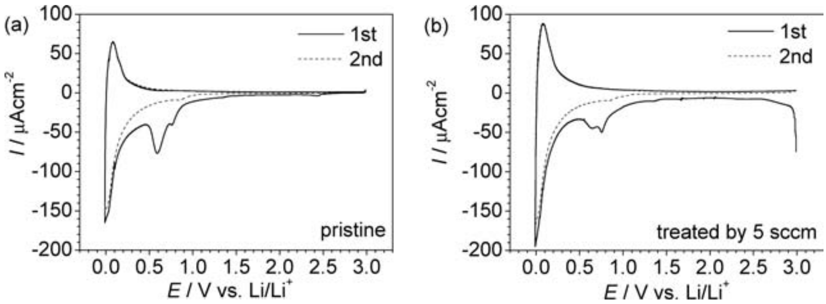

FIGURE 2 Cyclic voltammograms of carbonaceous thin films treated by NF_3 plasma: (a) pristine and (b) treated by 5 sccm.

are much higher than that of pristine film (ca. 3.2 V), which results in the fluorine atoms bonded to the carbonaceous thin film. After the 1st sweep, the OCP becomes almost the same as that of pristine film, which indicates that the fluorine atom on the film is reduced at the 1st sweep.

From the above results, fluorine atoms bonded to the carbonaceous thin film should act as a passivation layer (such as LiF) by the reaction with Li [20], which suppresses the reduction of solvent taking place at 0.6 V. However, the reduction of solvent taking place at 0.8 V was not suppressed by the surface treatment. Hence, reduction of the solvent should be responsible for passivation layer formed at 0.8 V.

CONCLUSION

Carbonaceous thin films prepared by plasma CVD were treated by NF_3 plasma to give surface fluorinated films. The degree of fluorination evaluated by AES was dependent on the flow rates of NF_3. From cyclic voltammograms, the decomposition of solvent at the 1st reduction process was suppressed by the fluorination. In addition, plasma treatment gave no change to the bulk electrochemical characteristics of carbonaceous thin films. It is concluded that surface modification of carbonaceous thin film by NF_3 plasma affects on the reduction of solvent in the lithium ion batteries.

REFERENCES

[1] Winter, M., Besenhard, J. O., Spahr, M. E., & Novák, P. (1998). *Adv. Mater.*, *10*, 725.

[2] Ogumi, Z. & Inaba, M. (1998). *Bull. Chem. Soc. Jpn.*, *71*, 521.

[3] Dahn, J. R., Zheng, T., Liu, Y., & Xue, J. S. (1995). *Science*, *270*, 590.

[4] Imanishi, N., Kashiwagi, H., Ichikawa, T., Takeda, Y., Yamamoto, O., & Inagaki, M. (1993). *J. Electrochem. Soc.*, *140*, 315.

[5] Mochida, I., Ku, C.-H., Yoon, S.-H., & Korai, Y. (1998). *J. Power Sources*, *75*, 214.

[6] Zheng, T., Xue, J. S., & Dahn, J. R. (1996). *Chem. Mater.*, *8*, 389.

[7] Inaba, M., Yoshida, H., Ogumi, Z., Abe, T., Mizutani, Y., & Asano, M. (1995). *J. Electrochem. Soc.*, *142*, 20.

[8] Inaba, M., Yoshida, H., & Ogumi, Z. (1996). *J. Electrochem. Soc.*, *143*, 2572.

[9] Han, Y.-S., Yu, J.-S., Park, G.-S., & Lee, J.-Y. (1999). *J. Electrochem. Soc.*, *146*, 3999.

[10] Inaba, M., Fujikawa, M., Abe, T., & Ogumi, Z. (2000). *J. Electrochem. Soc.*, *147*, 4008.

[11] Peled, E., Menachem, C., Bar-Tow, D., & Melman, A. (1996). *J. Electrochem. Soc.*, *143*, L4.

[12] Nakajima, T., Koh, M., Singh, R. N., & Shimada, M. (1999). *Electrochim. Acta*, *44*, 2879.

[13] Yoshio, M., Wang, H., Fukuda, K., Hara, Y., & Adachi, Y. (2000). *J. Electrochem. Soc.*, *147*, 1245.

[14] Abe, T., Fukutsuka, T., Inaba, M., & Ogumi, Z. (1999). *Carbon*, *37*, 1165.

[15] Fukutsuka, T., Abe, T., Inaba, M., & Ogumi, Z. (1999). *Tanso*, *190*, 252.

[16] Fukutsuka, T., Abe, T., Inaba, M., & Ogumi, Z. (2000). *Mol. Cryst. Liq. Cryst.*, *340*, 517.

[17] Fukutsuka, T., Abe, T., Inaba, M., Ogumi, Z., Matsuo, Y., & Sugie, Y. (2001). *Carbon Science*, *1*, 129.

[18] Fukutsuka, T., Abe, T., Inaba, M., & Ogumi, Z. (2001). *J. Electrochem. Soc.*, *148*, A1260.

[19] Matsuo, Y. & Nakajima, T. (1995). *Z. Anorg. Allg. Chem.*, *621*, 1943.

[20] Nakajima, T. (1999). *J. Fluorine Chem.*, *100*, 57.