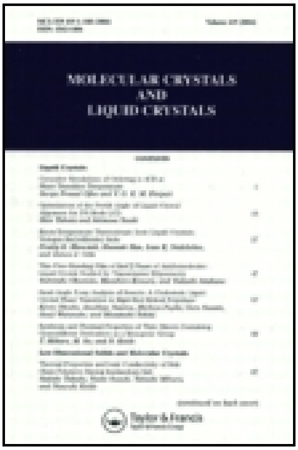

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Surface Structure And Electrochemical Characteristics Of Graphite Fluorinated By Elemental Fluorine And Plasma Treatment Using Cf 4

Tsuyoshi Nakajima [a], Vinay Gupta [a], Yoshimi Ohzawa [a], Hiroyuki Iwata [b], Alain Tressaud [c] & Etinne Durand [c]

[a] Department of Applied Chemistry, Aichi Institute of Technology, Toyota-shi, 470-0392, Japan

[b] Technical Research Center, Aichi Institute of Technology, Toyota-shi, 470-0392, Japan

[c] ICMCB-CNRS, Université Bordeaux I, Pessac Cedex, 33608, France

Version of record first published: 18 Oct 2010

To cite this article: Tsuyoshi Nakajima, Vinay Gupta, Yoshimi Ohzawa, Hiroyuki Iwata, Alain Tressaud & Etinne Durand (2002): Surface Structure And Electrochemical Characteristics Of Graphite Fluorinated By Elemental Fluorine And Plasma Treatment Using Cf 4, Molecular Crystals and Liquid Crystals, 388:1, 103-108

To link to this article: http://dx.doi.org/10.1080/713738879

*Mol. Cryst. Liq. Cryst.*, Vol. 388, pp. [517]/103–[522]/108
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113943

# SURFACE STRUCTURE AND ELECTROCHEMICAL CHARACTERISTICS OF GRAPHITE FLUORINATED BY ELEMENTAL FLUORINE AND PLASMA TREATMENT USING $CF_4$

*Tsuyoshi Nakajima, Vinay Gupta, and Yoshimi Ohzawa*
*Department of Applied Chemistry,*
*Aichi Institute of Technology,*
*Toyota-shi 470-0392, Japan*

*Hiroyuki Iwata*
*Technical Research Center, Aichi Institute of Technology,*
*Toyota-shi 470-0392, Japan*

*Alain Tressaud and Etinne Durand*
*ICMCB-CNRS, Université Bordeaux I,*
*33608 Pessac Cedex, France*

*Surface modification of graphite powder has been performed by elemental fluorine and radiofrequency plasma fluorination. Both of the methods enlarge the surface areas of graphite samples and change their pore volume distribution. Surface-fluorinated graphite samples demonstrate the capacities higher than those of original samples and even the theoretical capacity of graphite, 372 $mAhg^{-1}$ without reducing the first coulombic efficiencies. The increments of the capacities are ~5, ~10 and ~15% for graphite samples with average particle diameters of 7, 25 and 40 μm, respectively.*

*Keywords*: surface fluorination; surface structure; lithium ion battery; graphite electrode

## INTRODUCTION

Since the electrochemical redox reactions occur at the surface of electrode, structural factors such as crystallinity, surface area and surface pore volume distribution, and nature of surface chemical species are the

---

The present study was financially supported by grant-in-aid for Research for the Future Program (nanocarbon) of Japan Society for the Promotion of Science (JSPS). The fluorine gas was supplied by Daikin Industries Ltd. The authors would like to gratefully acknowledge them.

important factors affecting the electrode characteristics of carbon materials. Some methods of surface modification such as surface oxidation, metal coating and carbon coating were recently applied to carbonaceous electrodes to improve the electrode kinetics [1–10]. Surface fluorination by elemental fluorine and radiofrequency plasma fluorination using $CF_4$ is an effective method to improve the electrode characteristics of graphite [4–7]. In the present paper, we report the electrochemical properties of surface-fluorinated graphite samples and discuss about the relationship between the electrochemical results and surface structures of fluorinated samples.

## EXPERIMENTAL

Surface fluorination of graphite samples ($\approx$7, $\approx$25 and $\approx$40 µm) was performed between 128 and 500°C by elemental fluorine of $3 \times 10^4$ Pa for 2 min in a nickel reactor. The same graphite samples were also subjected to plasma fluorination using $CF_4$.

The surface fluorinated graphite samples were analyzed by elemental analysis of carbon and fluorine, X-ray diffractometry, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and surface area and pore volume distribution measurements.

The galvanostatic charge/discharge cycling for surface fluorinated samples was performed at 25°C using three electrodes glass cell. The counter and reference electrodes were metallic lithium, and electrolyte solution was 1 moldm$^{-3}$-$LiClO_4$-ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 in volume). The charge/discharge cycling was made at 60 mAg$^{-1}$ between 0 and 3 V vs Li/Li$^+$.

## RESULTS AND DISCUSSION

### Change in the Composition and Surface Structure of Graphite by Fluorination

The fluorine contents in surface-fluorinated graphite samples, obtained by elemental analysis, are less than 1 at% except the samples fluorinated between 350 and 500°C [5,7]. The fluorine contents in the samples fluorinated between 150 and 300°C are $0.2 \sim 0.4$ at% while the samples fluorinated between 350 and 500°C have the larger values, i.e., $0.6 \sim 4.7$ at%. On the other hand, the plasma-fluorinated samples show the lower fluorine contents, i.e., $0 \sim 0.3$ at% [6]. The value of zero indicates that the fluorine content is within detection limit.

The surface fluorine concentrations obtained by XPS have the same temperature dependency. The samples fluorinated between 150 and 300°C show 3.6 ~ 12.0 at%. On the other hand, the plasma-fluorinated samples exhibit rather constant surface fluorine concentrations less than 10 at% in most of the cases. The binding energies of C1s and F1s peaks indicate that the C-F bonding of surface-fluorinated graphite samples is in an intermediate state between the semi-ionic and covalent bonds [5–7,12–16].

The intensity of D-band in Raman spectrum is slightly enhanced by surface fluorination, indicating the increase in the surface disordering. The intensity ratio of two peaks, $R(=I_D/I_G)$, shows the degree of surface disordering of graphite powder. The results indicate that R values increase by surface fluorination, in particular, with increasing fluorination temperature and particle size of graphite powder. Plasma fluorination also increases the R values.

Figure 1 shows a transmission electron microscopic image of graphite sample fluorinated by plasma treatment. The fluorinated layers exhibit disordered structures in contrast with the unreacted graphene layers. The thickness of fluorinated layers is about 1 ~ 2 nm while the thickness is about 3 ~ 4 nm for the samples fluorinated by elemental fluorine, corresponding to 5 ~ 7 fluorine-intercalated layers [11–13].

The surface areas are enlarged by the fluorination using elemental fluorine, increasing with increase in the fluorination temperature for three kinds of graphite samples as given in Table 1. The increments of the surface areas are in the range of 64 ~ 77%. The surface areas of plasma-fluorinated samples are also increased by 26 ~ 55%. Fluorination of graphite powder

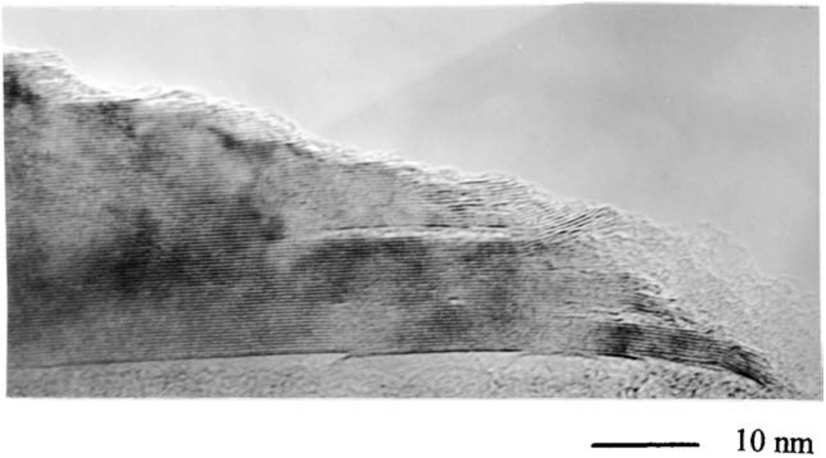

**FIGURE 1** Transmission electron micrograph of plasma-fluorinated graphite (≈40 μm).

**TABLE 1** Surface Areas of Surface-Fluorinated Graphite Samples, Measured by BET Method

| | Surface area ($m^2g^{-1}$) | | |
|---|---|---|---|
| Graphite | ≈7 μm | ≈25 μm | ≈40 μm |
| Original graphite | 4.79 | 3.71 | 2.94 |
| Fluorinated by $F_2$ | | | |
| 150°C | 5.61 | 5.16 | 3.50 |
| 250°C | 7.65 | 5.18 | 4.90 |
| 350°C | 8.48 | 6.09 | 4.95 |
| Plasma-fluorinated | 7.42 | 4.71 | 3.69 |

reduces the mesopores with the larger diameters and increases those with the diameters of 1.5 ~ 2 and 2 ~ 3 nm.

## Electrochemical Behavior of Surface-Fluorinated Graphite Samples

All the surface fluorinated samples show the higher capacities than original graphites. The capacities of surface-fluorinated samples (~25 μm) are higher than even the theoretical value of graphite, 372 $mAhg^{-1}$ except those of the samples fluorinated at 450 and 500°C. The samples fluorinated between 200 and 300°C give the highest capacities of 387 ~ 389 $mAhg^{-1}$ at 10th cycle. The increments of the charge capacities at 10th cycle are ~10%. The surface fluorinated graphite samples with average particle diameter of 7 μm show 378 ~ 383 $mAhg^{-1}$ higher than the theoretical capacity of graphite in most of the cases [5]. The increments of the capacities are ~5%. The surface-fluorinated samples (≈40 μm) fluorinated between 150 and 300°C exhibit the capacities of 374 ~ 377 $mAhg^{-1}$ slightly higher than the theoretical value of graphite at 10th cycle. The increments of the capacities at 10th cycle are ~13%.

Plasma fluorination using $CF_4$ is also very effective for increasing the capacity of graphite electrode [6]. The capacities of 60 min-fluorinated samples (≈25 μm) are in the range of 385 ~ 390 $mAhg^{-1}$ higher than that of original graphite and even the theoretical value, 372 $mAhg^{-1}$ as shown in Figure 2. In case of other 60 min plasma-fluorinated graphite samples with average particle diameters of 7 and 40 μm, the capacities are in the range of 377 ~ 384 and 372 ~ 382 $mAhg^{-1}$, respectively [6]. The increments of the capacities reach ~5, ~10 and ~15% for 7, 25 and 40 μm, respectively.

The fluorine contents are in the range of 0.2 ~ 0.4 at% and 0 ~ 0.3 at% for the samples fluorinated by elemental fluorine between 150 and 300°C and plasma-fluorinated samples, respectively. In these samples, no decrease

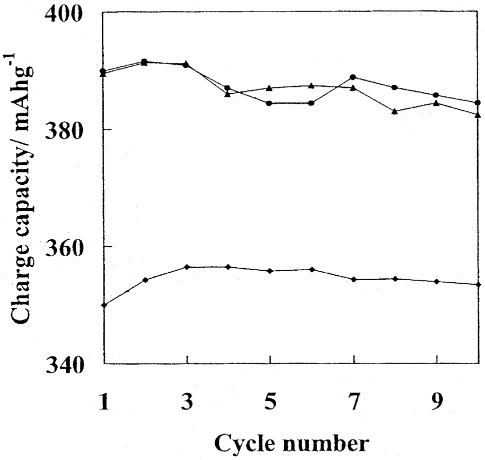

**FIGURE 2** Charge capacities of plasma-fluorinated graphite samples. ◆:original graphite (≈25 μm), ●:60 min-fluorinated sample at room temperature, ▲:60 min-fluorinated sample at 90°C.

in the first coulombic efficiencies is observed. It means that such amounts of fluorine are negligible.

The surface fluorination causes carbon-carbon bond breaking of graphite, increasing the surface areas of graphite samples and the mesopores with diameters of 1.5 ~ 2 and 2 ~ 3 nm, in which excess lithium exceeding the theoretical capacity would be stored.

## REFERENCES

[1] Peled, E., Menachem, C., Bar-Tow, D., & Melman, A. (1996). *J. Electrochem. Soc.*, *143*, L4.
[2] Hara, M., Satoh, A., Tamaki, N., & Ohsaki, T. (1994). *Tanso*, *165*, 261.
[3] Xue, J. S. & Dahn, J. R. (1995). *J. Electrochem. Soc.*, *142*, 3668.
[4] Nakajima, T. & Yanagida, K. (1996). *Tanso*, *174*, 195.
[5] Nakajima, T., Koh, M., Singh, R. N., & Shimada, M. (1999). *Electrochim. Acta*, *44*, 2879.
[6] Nakajima, T., Gupta, V., Ohzawa, Y., Koh, M., Singh, R. N., Tressaud, A., & Durand, E. *J. Power Sour.* in press.
[7] Gupta, V., Nakajima, T., Ohzawa, Y., & Iwata, H. *J. Fluorine Chem.*, in press.
[8] Takamura, T. & Kikuchi, M. (1995). *Battery Tech.*, *7*, 29.
[9] Takagi, R., Okubo, T., Sekine, K., & Takamura, T. (1997). *Denki Kagaku*, *65*, 333.
[10] Yoshio, M., Wang, H., Fukuda, K., Hara, Y., & Adachi, Y. (2000). *J. Electrochem. Soc.*, *147*, 1245.
[11] Watanabe, N., Nakajima, T., & Touhara, H. (1988). *Graphite fluorides*, Elsevier: Amsterdam.
[12] Nakajima, T. & Watanabe, N. (1991). *Graphite fluorides and carbon-fluorine compounds*, CRC Press: Boca Raton.

[13] Nakajima, T. (1995). Synthesis, structure, and physicochemical properties of fluorine-graphite intercalation compounds. In: ***Fluorine-Carbon and Fluoride-Carbon Materials: Chemistry, Physics and Applications***, Nakajima, T. (Ed.), Marcel Dekker: New York, 1–31.

[14] Palchan, I., Crespin, M., Estrade-Szwarckopf, H., & Rousseau, B. (1989). ***Chem. Phys. Lett.***, ***157***, 321.

[15] Tressaud, A., Guimon, C., Gupta, V., & Moguet, F. (1995). ***Mater. Sci. Eng.***, ***B30***, 61.

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