

ELECTROCHEMICAL PROPERTIES OF SURFACE-FLUORINATED VAPOR GROWN CARBON FIBER FOR LITHIUM ION BATTERY

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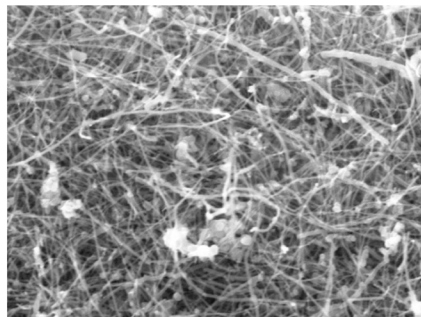
Dedicated to Professor Oldřich Paleta on the occasion of his 70th birthday.

Surface fluorination of graphitized vapor grown carbon fiber (VGCF) has been performed with F₂, F₂-O₂, NF₃ or ClF₃ under mild conditions. Charge/discharge characteristics were investigated in 1 mol/l LiClO₄-ethylene carbonate (EC)/diethyl carbonate (DEC) and EC/DEC/propylene carbonate (PC) solutions. The main effect of surface fluorination was increase in charge capacities. The increase in charge capacities was larger for VGCF fluorinated with ClF₃ or NF₃ than F₂ or F₂-O₂. The reason is that the fluorination reactions of graphite with ClF₃ and NF₃ are radical reactions having surface etching effect, effectively breaking cylindrically rolled graphene layers of VGCF.

Keywords: Surface modification; Chemical vapor deposition; Fluorination; Graphite anode; Lithium ion battery; Carbon electrodes.

Lithium ion batteries are used as electric sources for many kinds of electronic devices such as personal computers, mobile phones, cameras etc. To avoid dendrite formation, graphite is normally used as a host accommodating metallic lithium. Graphite has several advantages as an anode material

such as low potential, small irreversible capacity, good cycleability and constant capacity (theoretical capacity: 372 mAh/g corresponding to the stage 1 LiC_6). Recently the demand on high rate rechargeable batteries for the application to hybrid and electric cars has rapidly increased. Several methods such as surface modification, preparation of composites etc. have been attempted to improve electrode characteristics. Surface modification is one of the effective methods for such purpose¹⁻⁴⁵. Among the methods of surface modification (carbon coating⁵⁻¹², metal or metal oxide coating¹³⁻¹⁸, polymer or Si coating¹⁹⁻²⁶, surface oxidation²⁷⁻³¹ and surface fluorination³²⁻⁴⁵), surface fluorination using F_2 , ClF_3 or NF_3 gas and plasma fluorination using CF_4 effectively improve the electrode characteristics of graphitic materials such as natural and synthetic graphites by changing the surface structure, i.e. surface area, meso-pore size distribution, surface disorder, lattice defect and surface chemical species. Fluorination is a strong oxidation reaction, which can easily modify the surface structure of graphite with high crystallinity. The effect of surface fluorination varies depending on fluorinating agent or method, fluorination condition and crystallinity of carbon materials. Surface fluorination with F_2 is an electrophilic reaction, yielding surface-fluorinated layers⁴⁶⁻⁴⁸. On the other hand, surface fluorination with ClF_3 and NF_3 is a radical reaction showing surface etching effect. In the case of ClF_3 , a small amount of F_2 coexists in ClF_3 at high temperatures above 200 °C by partial dissociation of ClF_3 into ClF and F_2 ⁴⁹⁻⁵¹. Plasma fluorination is also a radical reaction, however, sample temperature is normally low. Vapor-grown carbon fibers (VGCF) are prepared by the chemical vapor deposition (CVD) using Fe catalyst (Fig. 1), currently employed as an additive for graphite anodes of lithium ion batteries⁵²⁻⁵⁴. VGCF has cylindrical-



2 μm

FIG. 1
SEM image of original VGCF

ly rolled graphene sheets in which intercalation of molecules and/or ions easily occurs. Graphitized VGCF was often used as a host for various graphite intercalation compounds because of its high crystallinity⁵⁵. Addition of graphitized VGCF to graphite anode enables good electric contact among graphite particles, improving the utilization of the available capacity of graphite and cycleability^{56,57}. VGCF not only provides electric contact to graphite particles as a binder, but also acts as an anode material accommodating Li^+ ions. Preliminary charge/discharge experiments have shown that graphitized VGCF has an unexpectedly small capacity as an anode material, which may be due to the structure of VGCF having cylindrically rolled graphene layers. It is expected that the electrode characteristics of VGCF improves if the surface structure changes by fluorination. In this study, graphitized VGCF was fluorinated using several different fluorinating agents. The charge/discharge behavior of surface-fluorinated VGCF was investigated.

RESULTS AND DISCUSSION

Surface Structure Change of VGCF by Fluorination

TEM images of original and surface-fluorinated VGCF samples are shown in Fig. 2. The VGCF sample consists of thin fibers with diameters of 40–100 nm (Fig. 2a) and each fiber has cylindrically rolled graphene layers with a small hole. Some fibers are mechanically broken. The surfaces of VGCF samples fluorinated with F_2 or $\text{F}_2\text{-O}_2$ (Figs 2c and 2d) were nearly the same as those of original VGCF though they had thin surface C–F layers as shown later. On the other hand, VGCF samples fluorinated with NF_3 and ClF_3 showed disordered surfaces (Figs 2e and 2f). It is seen in Fig. 2e that the top of the fiber was disordered by fluorination with NF_3 and in Fig. 2f that the fiber had disordered surface.

Surface compositions of fluorinated VGCF samples, obtained by XPS, are summarized in Table I. Surface fluorine concentrations are different depending on the fluorinating agents. Surface fluorine was clearly detected and its content increased with increasing temperature in VGCF samples fluorinated by F_2 or $\text{F}_2\text{-O}_2$, while no fluorine was found in most of the samples fluorinated with NF_3 and ClF_3 . The reaction of F_2 with carbon materials at temperatures lower than 500 °C is an electrophilic reaction giving surface C–F layers^{44,46–48}. However, the reactions of NF_3 and ClF_3 with carbon materials are radical reactions causing surface etching. In the case of ClF_3 , the

dissociation equilibrium: $\text{ClF}_3 \rightleftharpoons \text{ClF} + \text{F}_2$ exists at high temperatures (dissociation rates are 1.75% at 250 °C, 4.95% at 300 °C, 11.95% at 350 °C and 50% at 460 °C)⁴⁹⁻⁵¹. Therefore ClF_3 is actually a mixture of ClF_3 , ClF and F_2 at high temperatures above 250 °C. However, the experimental results show that radical reaction is dominant in fluorination of graphite with ClF_3 at 200–500 °C. Binding energies of F 1s electrons were in the range of 687–688 eV indicating C–F covalent bond. Surface oxygen concentrations were reduced except for VGCF samples fluorinated with $\text{F}_2\text{-O}_2$ at 400 and 500 °C. In addition, trace amounts of Cl were detected when the samples were fluorinated with ClF_3 at 400 and 500 °C.

TABLE I
Surface composition (in %) of VGCF samples fluorinated with F_2 , $\text{F}_2\text{-O}_2$, NF_3 and ClF_3

F_2				$\text{F}_2\text{-O}_2$					
Reaction temperature, °C	C	O	F	Reaction temperature, °C	C	O	F		
original	95.4	4.6	–	original	95.4	4.6	–		
150	94.4	3.8	1.8	200	94.8	4.1	1.1		
200	93.4	4.4	2.2	300	95.4	3.1	1.5		
300	88.6	3.3	8.1	400	93.6	4.7	1.7		
400	77.9	2.5	19.6	500	87.2	6.4	6.4		
NF_3					ClF_3				
Reaction temperature, °C	C	O	F	N	Reaction temperature, °C	C	O	F	Cl
original	95.4	4.6	–	–	original	95.4	4.6	–	–
200	96.7	3.3	N.D.	N.D.	200	97.9	2.1	N.D.	N.D.
300	96.2	3.2	0.6	N.D.	300	97.4	2.6	N.D.	N.D.
400	97.0	3.0	N.D.	N.D.	400	96.3	3.2	N.D.	0.5
500	96.8	2.6	0.6	N.D.	500	95.2	4.5	N.D.	0.3

Surface structure changes due to fluorination also differ depending on the fluorination mechanisms as shown in Table II. Surface disorder is evaluated by the R value ($R = I_D/I_G$) calculated from the peak intensity ratio of D-band (1360 cm^{-1}) to G-band (1580 cm^{-1}) in Raman spectra of carbon materials. Since the D-band intensity increases with increasing disorder, the R value is a good measure showing surface disorder. As shown in Table II, R values increased when VGCF was fluorinated with F_2 or F_2-O_2 while they did not change when fluorinated with NF_3 and ClF_3 . This means that the surface disorder of VGCF increased due to the fluorination with F_2 or F_2-O_2 , but did not change in the fluorination with NF_3 and ClF_3 . Surface areas slightly increased when VGCF was fluorinated with F_2 or F_2-O_2 , but decreased when fluorinated with NF_3 and ClF_3 . The decrease in the surface area was the largest when ClF_3 was used, which suggests that surface etching of VGCF surface was the strongest in the case of ClF_3 . Total pore volumes were also decreased by the fluorination with NF_3 and ClF_3 . These

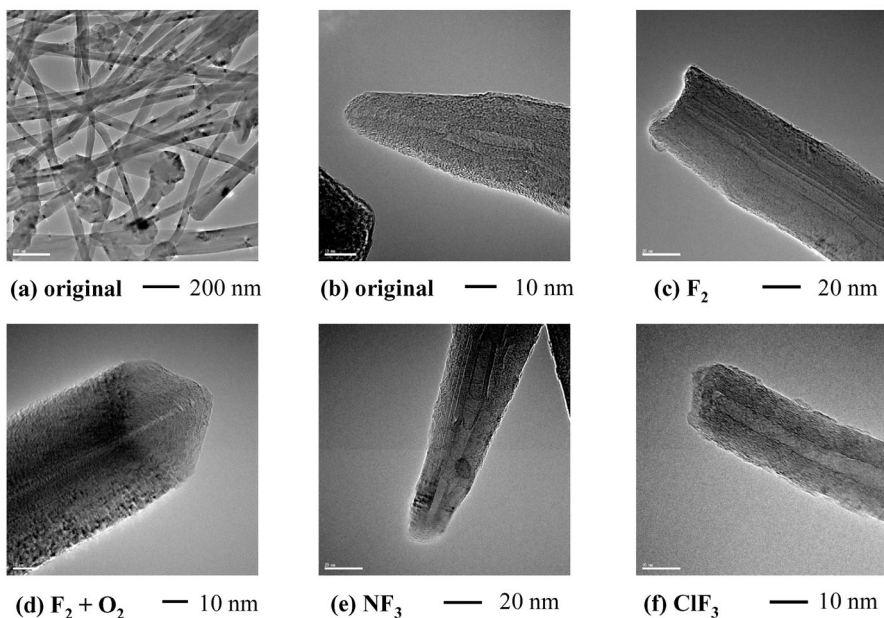


FIG. 2
TEM images of original and VGCF (a, b) samples surface-fluorinated with F_2 (c), F_2-O_2 (d), NF_3 (e) or ClF_3 (f) at $200\text{ }^\circ\text{C}$

surface structure changes are attributed to the difference in the reaction mechanisms: electrophilic reaction with F_2 yielding surface fluorinated layers or radical reactions with NF_3 and ClF_3 showing surface etching effect.

TABLE II
 R values (I_D/I_C), surface areas and pore volumes of VGCF samples fluorinated with F_2 , F_2-O_2 , NF_3 and ClF_3

F_2				F_2-O_2			
Reaction temperature, °C	R -value	Surface area m^2/g	Total pore volume cm^3/g	Reaction temperature, °C	R -value	Surface area m^2/g	Total pore volume cm^3/g
original	0.22	19.1	0.056	original	0.22	19.1	0.056
150	0.27	21.8	0.054	200	0.29	21.1	0.054
200	0.38	21.6	0.053	300	0.31	21.2	0.055
300	0.39	22.8	0.054	400	0.33	21.7	0.054
400	0.37	21.6	0.052	500	0.34	22.8	0.057
NF_3				ClF_3			
Reaction temperature, °C	R -value	Surface area m^2/g	Total pore volume cm^3/g	Reaction temperature, °C	R -value	Surface area m^2/g	Total pore volume cm^3/g
original	0.22	19.1	0.056	original	0.22	19.1	0.056
200	0.19	17.2	0.047	200	0.21	16.4	0.050
300	0.23	17.5	0.049	300	0.21	16.7	0.051
400	0.21	18.1	0.050	400	0.22	17.1	0.051
500	0.25	21.6	0.055	500	0.22	18.3	0.051

Charge/Discharge Characteristics of Surface-Fluorinated VGCF

First charge capacities and first coulombic efficiencies of original VGCF were 247 mAh/g and 70.0%, and 237 mAh/g and 66.2% at a current density of 60 mA/g in 1 mol/l $LiClO_4$ -EC/DEC and EC/DEC/PC, respectively. At the higher current density of 150 mA/g, they were 217 mAh/g and 71.9%, and 209 mAh/g and 70.1% in the same EC/DEC and EC/DEC/PC mixtures,

respectively (Tables III and IV). These values were much smaller than the theoretical value of graphite (372 mAh/g) as well as those for natural graphite samples with average particle sizes of 5, 10 and 15 μm (340, 317 and 295 mAh/g, respectively) reported in the previous paper⁴⁴. This is due to the VGCF consisting of cylindrically rolled graphene layers where Li^+ ion intercalation is more difficult than in graphite particles having a large area of edge planes. An interesting point is that first charge capacities and first Coulombic efficiencies were similar in both EC/DEC and EC/DEC/PC solvents. It is known that the formation of protective surface film (solid electrolyte interface: SEI) on graphite anode by electrochemical reduction of PC or EC is slower in PC-based than in EC-based solvents. When graphite anode is used in the PC-based solvent, a large irreversible capacity, i.e. a low first Coulombic efficiency is therefore observed. However, VGCF has

Table III

First charge/discharge capacities and first Coulombic efficiencies for VGCF samples fluorinated with F_2 , $\text{F}_2\text{-O}_2$, NF_3 and ClF_3 at 150 mA/g in 1 mol/l $\text{LiClO}_4\text{-EC/DEC}$ (1:1, vol.%)

F_2				$\text{F}_2\text{-O}_2$			
Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %	Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %
original	302	217	71.9	original	302	217	71.9
150	311	221	71.1	200	320	226	70.6
200	344	231	67.2	300	316	222	70.3
300	345	223	64.6	400	320	224	70.0
400	403	215	53.3	500	340	230	67.6
NF_3				ClF_3			
Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %	Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %
original	302	217	71.9	original	302	217	71.9
200	310	222	71.6	200	320	226	70.6
300	318	232	73.0	300	345	236	68.4
400	325	234	72.0	400	320	224	70.0
500	310	223	71.9	500	335	232	69.3

a large surface area (19.1 m²/g) as shown in Table II. Since charge/discharge experiments were made at a constant current density, a real current density decreased with increasing surface area, which means that the actual current density was relatively low in VGCF. Electrochemical decomposition of PC and subsequent formation of a surface film would be therefore easy on VGCF with a large surface area. The above result observed for VGCF is similar to that previously obtained for natural graphite with an average particle size of 5 μm (surface area: 13.9 m²/g)⁴⁴. First Coulombic efficiencies for 5 μm natural graphite were 81.4 and 81.8% in EC/DEC and EC/DEC/PC solvents, respectively⁴⁴.

To improve the charge/discharge behavior of VGCF, surface fluorination was performed using several fluorinating agents. No large difference in charge capacities and first Coulombic efficiencies was observed by surface

TABLE IV

First charge/discharge capacities and first Coulombic efficiencies for VGCF samples fluorinated with F₂, F₂-O₂, NF₃ and ClF₃ at 150 mA/g in 1 mol/l LiClO₄-EC/DEC/PC (1:1:1, vol.%)

F ₂				F ₂ -O ₂			
Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %	Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %
original	298	209	70.1	original	298	209	70.1
150	325	225	69.2	200	315	221	70.2
200	309	214	69.3	300	309	220	71.2
300	330	224	67.9	400	307	219	71.3
400	376	212	56.4	500	321	216	67.3
NF ₃				ClF ₃			
Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %	Temperature, °C	Discharge capacity mAh/g	Charge capacity mAh/g	Coulombic efficiency %
original	298	209	70.1	original	298	209	70.1
200	319	224	70.2	200	335	235	70.1
300	317	226	71.3	300	336	248	73.8
400	322	232	72.0	400	330	226	68.5
500	306	216	70.6	500	330	226	68.5

fluorination when fluorinated VGCF samples were examined at a current density of 60 mA/g. Difference in the charge/discharge characteristics was found at the higher current density of 150 mA/g. First Coulombic efficiencies for surface-fluorinated VGCF samples were nearly the same as those of original sample except several samples fluorinated with F_2 or F_2-O_2 at high temperatures as shown in Tables III and IV. This may be due to the large surface areas of all fluorinated samples even after surface fluorination. Interesting results were obtained with charge capacities. Charge capacities were increased by surface fluorination, particularly for the samples fluorinated with NF_3 and ClF_3 as shown in Figs 3 and 4. In the case of the sam-

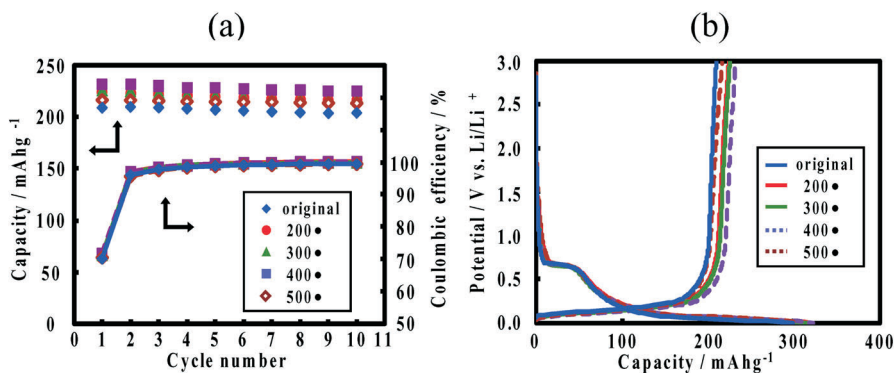


FIG. 3

Charge capacities and Coulombic efficiencies (a) and first charge/discharge curves (b) for VGCF samples fluorinated with NF_3 at 150 mA/g in 1 mol/l $LiClO_4$ -EC/DEC/PC (1:1:1, vol.%)

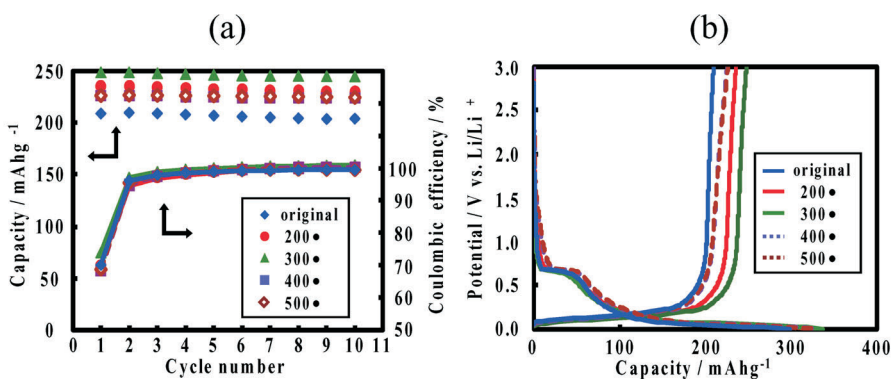


FIG. 4

Charge capacities and Coulombic efficiencies (a) and first charge/discharge curves (b) for VGCF samples fluorinated with ClF_3 at 150 mA/g in 1 mol/l $LiClO_4$ -EC/DEC/PC (1:1:1, vol.%)

ples fluorinated with F_2 or F_2-O_2 , the increase in the first charge capacities were ~ 7 and $\sim 6\%$, respectively, in both EC/DEC and EC/DEC/PC solvents (Tables III and IV). However, the increase in first charge capacities was larger when VGCF was fluorinated with NF_3 and ClF_3 showing surface etching effect. It is observed in Figs 3 and 4 that charge capacities increased on surface fluorination with NF_3 and ClF_3 . The increase in first charge capacities reached ~ 8 and $\sim 11\%$ in EC/DEC and EC/DEC/PC, respectively, for NF_3 -fluorinated samples. In surface fluorination using ClF_3 , the increase in first charge capacities was ~ 9 and $\sim 19\%$, in EC/DEC and EC/DEC/PC, respectively. The most effective fluorinating gas was therefore ClF_3 . The increase in first charge capacities was slightly larger in EC/DEC/PC than in EC/DEC particularly for the samples fluorinated by ClF_3 . TEM images in Fig. 2 show that ClF_3 and NF_3 effectively break cylindrically rolled graphene layers of VGCF by radical reactions, which makes easy the intercalation of Li^+ ion into VGCF, leading to the increase in charge capacities.

EXPERIMENTAL

Graphite samples were vapor grown carbon fibers (VGCFs) prepared using Fe catalyst and then heat-treated at $2800\text{ }^\circ\text{C}$ ($d_{002} = 0.3380\text{ nm}$). A SEM image of original VGCF with fibrous structure is shown in Fig. 1. Graphitized VGCFs were fluorinated with F_2 ($3 \times 10^4\text{ Pa}$) at $150\text{--}400\text{ }^\circ\text{C}$ for 2 min, with a mixture of F_2 ($3 \times 10^4\text{ Pa}$) and O_2 ($3 \times 10^4\text{ Pa}$) at $200\text{--}500\text{ }^\circ\text{C}$ for 2 min, with ClF_3 ($3 \times 10^4\text{ Pa}$) at $200\text{--}500\text{ }^\circ\text{C}$ for 3 min, or with NF_3 ($3 \times 10^4\text{ Pa}$) at $200\text{--}500\text{ }^\circ\text{C}$ for 3 min. VGCFs and fluorinated samples were characterized by X-ray diffractometry (XRD-6100, Shimadzu) with $CuK\alpha$ radiation, X-ray photoelectron spectroscopy (XPS) (ESCA-3400, Kratos) with $MgK\alpha$ radiation, Raman spectroscopy (NRS-1000, Jasco) with Nd:YVO₄ laser (532 nm), surface area measurement (Tristar 3000, Shimadzu), scanning electron microscopy (SEM) (Superscan SS-550, Shimadzu) and transmission electron microscopy (TEM) (JEM-2100F, JEOL).

Three electrode-cell with a VGCF sample as a working electrode and metallic lithium as counter and reference electrodes was used for galvanostatic charge/discharge cycling. The electrolyte solutions used were 1 mol/l $LiClO_4$ -EC/DEC (1:1, vol.%) and EC/DEC/PC (1:1:1, vol.%) (Kishida Chemicals, Co. Ltd., H_2O : 2–5 ppm). VGCF electrode was prepared as follows. A VGCF sample was dispersed in *N*-methyl-2-pyrrolidone (NMP) containing 12 wt.% poly(vinylidene fluoride) (PVdF) and the slurry was pasted on a copper current collector. The electrode was dried at $120\text{ }^\circ\text{C}$ under vacuum for half a day. After drying, the electrode contained 80 wt.% VGCF and 20 wt.% PVdF. Charge/discharge experiments were performed at current densities of 60 and 150 mA/g between 0 and 3 V relative to the Li/Li^+ reference electrode in a glove box filled with Ar at $25\text{ }^\circ\text{C}$ (Hokuto Denko, HJ1001 SM8A).

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REFERENCES

1. Takamura T.: *Bull. Chem. Soc. Jpn.* **2002**, 75, 21.
2. Ning L. J., Wu Y. P., Fang S. B., Rahm E., Holze R.: *J. Power Sources* **2004**, 133, 229.
3. Nakajima T. in: *Fluorinated Materials for Energy Conversion* (T. Nakajima and H. Groult, Eds), Chap. 2. Elsevier, Oxford 2005.
4. Fu L. J., Liu H., Li C., Wu Y. P., Rahm E., Holze R., Wu H. Q.: *Solid State Sci.* **2006**, 8, 113.
5. Yoshio M., Wang H., Fukuda K., Hara Y., Adachi Y.: *J. Electrochem. Soc.* **2000**, 147, 1245.
6. Wang H., Yoshio M.: *J. Power Sources* **2001**, 93, 123.
7. Yoon S., Kim H., Oh S. M.: *J. Power Sources* **2001**, 94, 68.
8. Wang H., Yoshio M., Abe T., Ogumi Z.: *J. Electrochem. Soc.* **2002**, 149, A499.
9. Yoshio M., Wang H., Fukuda K., Umeno T., Dimov N., Ogumi Z.: *J. Electrochem. Soc.* **2002**, 149, A1598.
10. Han Y.-S., Lee J.-Y.: *Electrochim. Acta* **2003**, 48, 1073.
11. Ohzawa Y., Yamanaka Y., Naga K., Nakajima K.: *J. Power Sources* **2005**, 146, 125.
12. Lee J.-H., Lee H.-Y., Oh S.-M., Lee S.-J., Lee K.-Y., Lee S.-M.: *J. Power Sources* **2007**, 166, 250.
13. Takamura T., Sumiya K., Suzuki J., Yamada C., Sekine K.: *J. Power Sources* **1999**, 81/82, 368.
14. Wu Y., Jiang C., Wan C., Tsuchida E.: *Electrochem. Commun.* **2000**, 2, 626.
15. Kim S.-S., Kadoma Y., Ikuta H., Uchimoto Y., Wakihara M.: *Electrochem. Solid-State Lett.* **2001**, 4, A109.
16. Lee J. K., Ryu D. H., Ju J. B., Shul Y. G., Cho B. W., Park D.: *J. Power Sources* **2002**, 107, 90.
17. Kottogoda I. R. M., Kadoma Y., Ikuta H., Uchimoto Y., Wakihara M.: *Electrochem. Solid-State Lett.* **2002**, 5, A275.
18. Kottogoda I. R. M., Kadoma Y., Ikuta H., Uchimoto Y., Wakihara M.: *J. Electrochem. Soc.* **2005**, 152, A1595.
19. Kuwabata S., Tsumura N., Goda S., Martin C. R., Yoneyama H.: *J. Electrochem. Soc.* **1998**, 145, 1415.
20. Gaberscek M., Bele M., Drogenik J., Dominko R., Pejovnik S.: *Electrochem. Solid-State Lett.* **2000**, 3, 171.
21. Drogenik J., Gaberscek M., Dominko R., Bele M., Pejovnik S.: *J. Power Sources* **2001**, 94, 97.
22. Bele M., Gaberscek M., Dominko R., Drogenik J., Zupan K., Komac P., Kocevar K., Musevic I., Pejovnik S.: *Carbon* **2002**, 40, 1117.
23. Gaberscek M., Bele M., Drogenik J., Dominko R., Pejovnik S.: *J. Power Sources* **2001**, 97/98, 67.
24. Veeraraghavan B., Paul J., Haran B., Popov B.: *J. Power Sources* **2002**, 109, 377.
25. Holzapfel M., Buqa H., Krumeich F., Novak P., Petrat F. M., Veit C.: *Electrochem. Solid-State Lett.* **2005**, 8, A516.

26. Endo K., Zhang H. P., Fu L. J., Lee K. J., K., Takamura T., Jeong Y. U., Wu Y. P., Holze R., Wu H. Q.: *J. Appl. Electrochem.* **2006**, *36*, 1307.
27. Peled E., Menachem C., Bar-Tow D., Melman A.: *J. Electrochem. Soc.* **1996**, *143*, L4.
28. Wu Y., Jiang C., Wan C., Tsuchida E.: *J. Mater. Chem.* **2001**, *11*, 1233.
29. Wu Y. P., Jiang C., Wan C., Holze R.: *Electrochem. Commun.* **2002**, *4*, 483.
30. Wu Y., Jiang C., Wan C., Holze R.: *J. Power Sources* **2002**, *111*, 329.
31. Wu Y. P., Jiang C., Wan C., Holze R.: *J. Appl. Electrochem.* **2002**, *32*, 1011.
32. Nakajima T., Koh M., Singh R. N., Shimada M.: *Electrochim. Acta* **1999**, *44*, 2879.
33. Gupta V., Nakajima T., Ohzawa Y., Iwata H.: *J. Fluorine Chem.* **2001**, *112*, 233.
34. Nakajima T., Gupta V., Ohzawa Y., Koh M., Singh R. N., Tressaud A., Durand E.: *J. Power Sources* **2002**, *104*, 108.
35. Groult H., Nakajima T., Perrigaud L., Ohzawa Y., Yashiro H., Komaba S., Kumagai N.: *J. Fluorine Chem.* **2005**, *126*, 1111.
36. Nakajima T., Li J., Naga K., Yoneshima K., Nakai T., Ohzawa Y.: *J. Power Sources* **2004**, *133*, 243.
37. Li J., Naga K., Ohzawa Y., Nakajima T., Shames A. P., Panich A. I.: *J. Fluorine Chem.* **2005**, *126*, 265.
38. Li J., Ohzawa Y., Nakajima T., Iwata H.: *J. Fluorine Chem.* **2005**, *126*, 1028.
39. Naga K., Nakajima T., Ohzawa Y., Žemva B., Mazej Z., Groult H.: *J. Electrochem. Soc.* **2007**, *154*, A347.
40. Naga K., Nakajima T., Aimura S., Ohzawa Y., Žemva B., Mazej Z., Groult H., Yoshida A.: *J. Power Sources* **2007**, *167*, 192.
41. Nakajima T., Shibata S., Naga K., Ohzawa Y., Tressaud A., Durand E., Groult H., Warmont F.: *J. Power Sources* **2007**, *168*, 265.
42. Groult H., Nakajima T., Tressaud A., Shibata S., Durand E., Perrigaud L., Warmont F.: *Electrochem. Solid-State Lett.* **2007**, *10*, A212.
43. Matsumoto K., Li J., Ohzawa Y., Nakajima T., Mazej Z., Žemva B.: *J. Fluorine Chem.* **2006**, *127*, 1383.
44. Achiha T., Nakajima T., Ohzawa Y.: *J. Electrochem. Soc.* **2007**, *154*, A827.
45. Achiha T., Shibata S., Nakajima T., Ohzawa Y., Tressaud A., Durand E.: *J. Power Sources* **2007**, *171*, 932.
46. Rozen S., Gal C.: *Tetrahedron Lett.* **1984**, *25*, 449.
47. Rozen S., Gal C.: *J. Fluorine Chem.* **1985**, *27*, 143.
48. Koh M., Yumoto H., Higashi H., Nakajima T.: *J. Fluorine Chem.* **1999**, *97*, 239.
49. Ruff O., Krug H.: *Z. Anorg. Allg. Chem.* **1930**, *190*, 270.
50. Grisard J. W., Bernhard H. A., Oliver G. D.: *J. Am. Chem. Soc.* **1951**, *73*, 5725.
51. Mellor J. W. (Ed.): *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Suppl. II, Part I, p. 147. Longman, Green and Co., London 1956.
52. Endo M., Takeuchi K., Kobori K., Takahashi K., Kroto H. W., Sarkar A.: *Carbon* **1995**, *33*, 873.
53. Endo M., Takeuchi K., Hiraoka T., Furuta T., Kasai T., Sun X., Kiang C. H., Dresselhaus M. S.: *J. Phys. Chem. Solid* **1997**, *58*, 1707.
54. Endo M., Kim Y. A., Takeda T., Hong S. H., Matusita T., Hayashi T., Dresselhaus M. S.: *Carbon* **2001**, *39*, 2003.
55. Dresselhaus M. S., Dresselhaus G.: *Adv. Phys.* **1981**, *30*, 139.
56. Endo M., Kim Y. A., Hayashi T., Nishimura K., Matusita T., Miyashita K., Dresselhaus M. S.: *Carbon* **2001**, *39*, 1287.
57. Endo M.: *Mol. Cryst. Liq. Cryst.* **2002**, *386*, 159.