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Review

Surface modification of carbon anodes for secondary lithium battery by fluorination

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Abstract

Recent results on the surface modification of petroleum cokes and their electrochemical properties as anodes of secondary lithium batteries are summarized. The surface of petroleum coke and those heat-treated at 1860–2800 °C were fluorinated by elemental fluorine (F_2), chlorine trifluoride (ClF_3) and nitrogen trifluoride (NF_3). No surface fluorine was found except only one sample when ClF_3 and NF_3 were used as fluorinating agents while surface region of petroleum coke was fluorinated when F_2 was used. Transmission electron microscopic (TEM) observation revealed that closed edge of graphitized petroleum coke was destroyed and opened by surface fluorination. Raman spectra showed that surface fluorination increased the surface disorder of petroleum cokes. Main effect of surface fluorination with F_2 is the increase in the first coulombic efficiencies of petroleum cokes graphitized at 2300–2800 °C by 12.1–18.2% at 60 mA/g and by 13.3–25.8% at 150 mA/g in 1 mol/dm^3 $LiClO_4$–ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v). On the other hand, main effect of the fluorination with ClF_3 and NF_3 is the increase in the first discharge capacities of graphitized petroleum cokes by ~63 mAh/g (~29.5%) at 150 mA/g in 1 mol/dm^3 $LiClO_4$–EC/DEC.

Keywords: Surface modification; Fluorination; F_2; ClF_3; NF_3; Carbon anode; Secondary lithium battery

Contents

1. Introduction

The development and utilization of various batteries generating electric energy by chemical reactions are urgent issues for the suppression of global warming effect. Among them, the importance of secondary (rechargeable) lithium battery with high power density is increasing in application to hybrid cars. Since metallic lithium cannot be used as anode of secondary lithium battery due to the dendrite formation, graphite intercalation compound of lithium has been applied. Anode characteristics of various metal oxides and alloys have been also examined. However, their application to anode materials is for the moment difficult due to the large irreversible capacities. Graphite anodes generally have such advantages as low irreversible capacities (high first coulombic efficiencies), low discharge potentials and constant discharge capacities. The importance of fluorine chemistry is rapidly increasing in secondary lithium battery. Fluorine compounds

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are currently used in secondary lithium batteries as electrolytes, binder and so on [1]. Recent research interest is concerned with the application of fluorination techniques to electrode materials and organic solvents, and the synthesis of fluorine containing electrolytes and organic solvents [1]. Secondary lithium batteries need such properties as high reversible capacity, high first coulombic efficiency (low irreversible capacity), high cycleability and high rate characteristics. First columbic efficiency is associated with the irreversible capacity loss in the 1st cycle that involves electrolyte decomposition and subsequent formation of surface film (solid electrolyte interphase or interface: SEI) on carbonaceous anode. Some lithium ions are consumed by the formation of SEI, and therefore are not inserted in graphene layers. It is one of the important issues for the development of carbonaceous anodes how to suppress the electrochemical decomposition of solvents for the formation of SEI. Since electrochemical reactions take place at the surface of electrodes, surface structure is an important factor determining the electrochemical characteristics of carbon materials. It has been shown by the recent investigations that surface modification of carbon materials is an effective method to improve the electrochemical characteristics of carbonaceous electrodes [2]. Some methods of surface modification have been already applied. They are surface oxidation [3–5], surface fluorination [6–15], metal or metal oxide coating [16–19] and carbon coating [20–25]. It has been shown that surface fluorination increases the discharge capacities of natural graphite samples with different particle sizes [6–10]. Light fluorination of natural graphite powder by elemental fluorine increased surface areas and meso-pores with diameters of 2–3 nm, resulting in the increase in the discharge capacities without decrease in first coulombic efficiencies [6–8,10]. Plasma fluorination using CF_4 also gave the same results for natural graphite powder [9,10]. The larger discharge capacities than the theoretical value of graphite, 372 mAh/g were obtained for surface-fluorinated graphite samples [6–10]. Since synthetic graphites are often used as anodes of secondary lithium batteries, petroleum coke and those heat-treated at 1860–2800 °C were fluorinated by F_2, ClF_3 and NF_3 and their surface structure changes and electrochemical behavior were recently investigated [11–13,26]. The present paper summarizes the results recently obtained for the petroleum coke samples.

2. Surface structure change and electrochemical properties of surface-fluorinated petroleum cokes

2.1. Charge/discharge characteristics of non-fluorinated petroleum cokes

Table 1
First coulombic efficiencies of non-fluorinated petroleum cokes in 1 mol/dm^3 $LiClO_4$–EC/DEC at current densities of 60 and 150 mA/g

Current density (mA/g)	Sample					
	PC	PC1860	PC2100	PC2300	PC2600	PC2800
60	72.3	90.2	90.5	71.9	67.0	65.4
150	–	89.1	88.2	70.0	56.3	63.6

The starting carbon materials were petroleum coke and those heat-treated at 1860, 2100, 2300, 2600 and 2800 °C (abbreviated to PC, PC1860, PC2100, PC2300, PC2600 and PC2800). The *d*-spacings of (0 0 2) diffraction lines were 0.3450, 0.3385, 0.3376, 0.3366, 0.3362 and 0.3361 nm for PC, PC1860, PC2100, PC2300, PC2600 and PC2800, respectively. Potential curves for original petroleum coke (PC) gradually decreased and increased with intercalation and deintercalation of lithium ion, respectively. However, the profile of potential curves for petroleum cokes heat-treated at 2100–2800 °C was rather similar to that for natural graphite [11–13]. First coulombic efficiencies of non-fluorinated petroleum cokes varied depending on the heat-treatment temperatures, that is, the crystallinity of petroleum coke samples. Petroleum cokes heat-treated at 1860 and 2100 °C (PC1860 and PC2100) exhibited high first coulombic efficiencies, 90.5–88.2% at current densities of 60 and 150 mA/g. However, first coulombic efficiencies were decreased with increasing heat-treatment temperature of petroleum coke, that is, 71.9–70.0%, 67.0–56.3% and 65.4–63.6% for petroleum cokes heat-treated at 2300, 2600 and 2800 °C (PC2300, PC2600 and PC2800), respectively as given in Table 1. Transmission electron microscopic study revealed that edge plane of heat-treated carbon is closed by carbon–carbon bond formation as shown in Fig. 1 [13], which would give a difficulty to SEI formation and electrochemical insertion of lithium ion into carbon electrode. This may be the main reason why the first coulombic efficiencies of PC2300, PC2600 and PC2800 were lower than those for PC1860 and PC2100. Synthetic graphite is usually prepared by heat-treatment of a graphitizable carbon at 2800–3000 °C. During the graphitization process at high temperatures, surface oxygen is eliminated as CO accompanying carbon–carbon bond breaking. Since graphitization of a carbon is made in a reduced atmosphere, dangling carbon bonds are combined with each other, forming closed and round edge planes. TEM image of PC2800 shown in Fig. 1 is similar to that of top of carbon nanotube. However, the

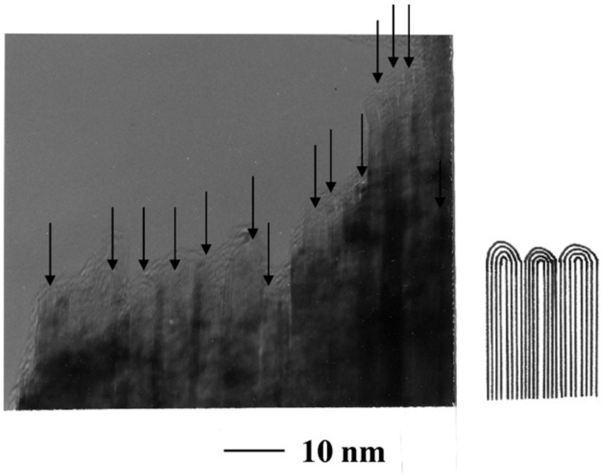

Fig. 1. TEM image of PC2800.

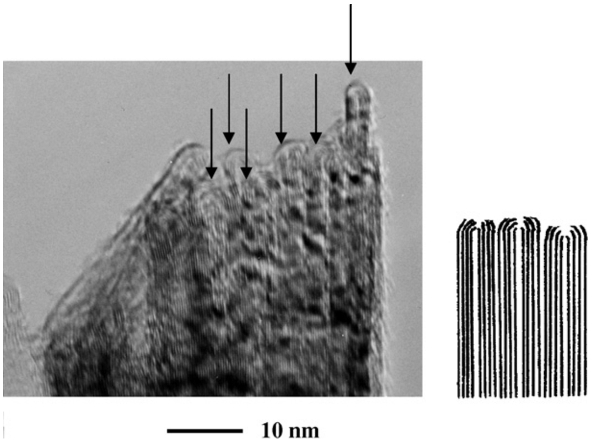

Fig. 2. TEM image (a) of PC2800 fluorinated by F_2 at 400 °C.

edge of petroleum coke is different from the top of carbon nanotube because petroleum coke has layered sheet structure. At the edge of PC2800, different graphene sheets are combined with each other, forming closed edge planes. When synthetic graphite is prepared, surface oxygen should be eliminated before heat-treatment and edge structure should be checked after graphitization. On the other hand, natural graphite powder is prepared by pulverizing flake graphite and sieving powder mixture with different particle sizes. Therefore the edge of natural graphite powder is opened though most of them may be terminated by oxygen.

2.2. Composition and surface structure change of petroleum cokes by fluorination

Surface fluorination of petroleum coke sample (about 150 mg) was made at 200 and 300 °C by F_2 of 3×10^4 Pa for 2 min, and at 200–500 °C by ClF_3 or NF_3 of 3×10^4 Pa for 2 min in a nickel reactor. Light fluorination of petroleum cokes effectively changes the surface structure. TEM observation clearly demonstrated the surface structure change of petroleum coke samples by fluorination. Figs. 2 and 3 show transmission electron microscopic images (TEM images) of PC2800 fluorinated by F_2 at 400 °C for 2 min. Edge of non-fluorinated PC2800 has many closed surfaces as shown in Fig. 1 [13]. The top of bended graphene sheets was somewhat lost in one part (Fig. 2) [13] and surface region was more highly fluorinated in another part by surface fluorination (Fig. 3) [27]. PC2800 fluorinated by ClF_3 and NF_3 show etched surface and opened edge [26]. The closed edge surface was thus destroyed and opened with carbon–carbon bond rupture.

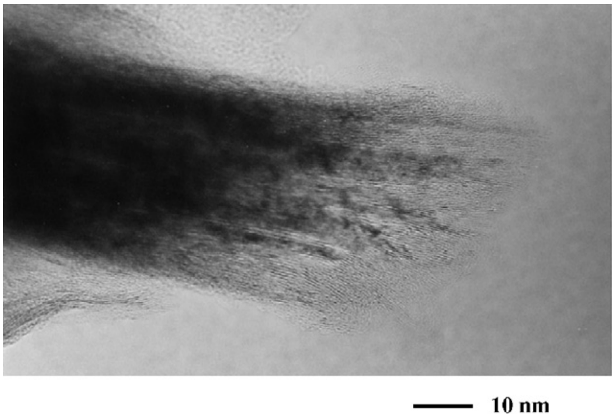

Fig. 3. TEM image (b) of PC2800 fluorinated by F_2 at 400 °C.

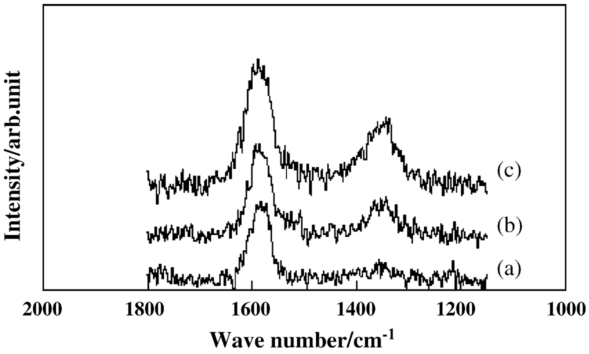

Fig. 4. Raman spectra of PC2600 (a) and those fluorinated at 200 °C (b) and 300 °C (c).

Raman spectroscopy reveals surface disorder of carbon materials [28,29]. Two Raman shifts are usually observed at 1580 and 1360 cm^{-1} indicating graphitic structure (E_{2g2} mode, G-band) and disordered structure (A_{1g} mode, D-band), respectively. Fig. 4 shows Raman spectra of PC2600 and those fluorinated by F_2 [13]. Intensity ratio of Raman shifts ($R = I_D/I_G$) is an important measure giving a degree of surface disorder. R values obtained from the intensity ratio of two Raman shifts for petroleum cokes and those fluorinated by F_2 are given in Table 2 [11–13]. R value for non-fluorinated petroleum coke decreased from 0.87 to 0.18 with increase in the heat-treatment temperature, i.e. with increase in the crystallinity of petroleum coke. It means that surface disorder of petroleum coke is significantly decreased by graphitization. It is clearly shown that surface fluorination enhances the peak intensity of D-band at 1360 cm^{-1} in any case. The result shows that surface disorder of petroleum coke samples was enhanced by light fluorination accompanying carbon–carbon bond breaking and probably simultaneous formation of CF_2/CF_3 groups in the surface region. The BET surface areas of petroleum cokes and those fluorinated by F_2 are summarized in Table 3 [11–13]. The surface area of PC is large, however, decreasing to half or less than half by heat-treatment. The meso-pore volumes were also decreased by heat-treatment in the same manner [11–13]. Surface area of PC was slightly increased by the fluorination at

Table 2
R values ($= I_D/I_G$) obtained from peak intensity ratios of Raman shifts for petroleum cokes and those fluorinated by F_2

	Petroleum coke					
	PC	PC1860	PC2100	PC2300	PC2600	PC2800
Non-fluorinated	0.87	0.49	0.36	0.21	0.17	0.18
Fluorinated at 300 °C	0.94	0.78	0.70	0.68	0.52	0.43

Table 3
BET surface areas (m^2/g) of petroleum cokes and those fluorinated by F_2

Fluorination temperature (°C)	Petroleum coke					
	PC	PC1860	PC2100	PC2300	PC2600	PC2800
Original	6.35	3.31	2.34	2.33	2.31	2.43
200	8.06	3.31	2.50	2.27	2.65	2.73
300	25.2	3.20	2.63	2.25	2.34	2.81

200 °C, and largely increased at 300 °C. A low crystalline carbon with a large surface area is easily fluorinated, forming covalently bonded C–F layers, though the highly disordered parts may be lost by the fluorination as CF_4 gas. Surface areas of the fluorinated PC1860, PC2100 and PC2300 were almost the same as or slightly smaller than those before fluorination. The meso-pore volumes had the similar trend [11–13]. Surface disordered parts were mainly eliminated in these samples. On the other hand, fluorination behavior of PC2800 is rather similar to that of natural graphite powder because the surface areas of PC2800 were enlarged by 12–17%. Main reaction would be the formation of C–F covalent bonds accompanying the carbon–carbon bond breaking, which results in the formation of CF_2/CF_3 groups. In case of the same petroleum cokes fluorinated by ClF_3 and NF_3 at 200 and 300 °C for 2 min, BET surface areas of all fluorinated samples were decreased after fluorination. It suggests that fluorination mechanism is different from that by F_2.

The results of elemental analysis of petroleum cokes fluorinated by F_2 are given in Table 4 [11–13]. Fluorine contents were relatively higher in PC, in particular in the sample fluorinated at 300 °C. Smaller amounts of fluorine were detected for all the heat-treated petroleum cokes. Fluorine contents in the heat-treated petroleum cokes fluorinated at 200 °C were within the detection limit (<0.2 at.%). This suggests that the reactivity of fluorine with petroleum cokes decreases with increasing heat-treatment temperature probably due to the closure of edge planes. The fluorine contents were in the range of 0.3–0.6 at.% for heat-treated petroleum cokes when fluorinated at 300 °C. Table 5 shows binding energies of C 1s, O 1s and F 1s electrons and surface composition of petroleum cokes and those fluorinated by F_2 at 300 °C [11–13]. The binding energies for F 1s electron are close to that for C–F covalent bond (binding energy of F 1s electron: 689–690 eV [30,31]), however, decreasing from 688.8 to 687.3 eV with decreasing surface fluorine probably due to the reduction of charging effect. Corresponding to the F 1s peaks, weak shifted peaks of C 1s electron were observed at 290.1–288.3 eV for fluorinated samples of PC, PC1860, PC2100 and PC2600. Heat-treatment of petroleum coke reduced the surface oxygen by 5.6 at.%. Fluorination further reduced the surface oxygen by 7.2–1.0 at.% as given in Table 5. The surface oxygen of natural graphite powder (≈7 μm) was 6 at.% when Shimadzu ESCA 1000 spectrometer was used [11]. However, it was 1.5–2.0 at.% when Ulvac Phi Model 5500 spectrometer was used before [6]. The difference in the amounts of surface oxygen may arise from the difference in the vacuum levels of the spectrometers. This suggests that the actual amounts of surface oxygen are about 4 at.% lower than those listed in Table 5, that is, those of non-fluorinated and fluorinated samples are estimated to be approximately in the range of 2.6–8.2 and 0.9–2.6 at.%, respectively. The amounts of surface fluorine significantly decreased from 50.2 to 5.2 at.% with increasing crystallinity of petroleum coke, which shows that the reactivity of F_2 with petroleum coke is lowered with increase in the crystallinity of petroleum coke.

Fluorination mechanism by ClF_3 and NF_3 is different from that by F_2 because no surface fluorine was detected by XPS except one sample as given in Table 6 [26]. In addition, small amounts of chlorine were detected in the samples fluorinated by ClF_3. Small amounts of nitrogen were also found in PC fluorinated by NF_3 at 200 and 300 °C. ClF_3 has a boiling point of 11.75 °C and its vapor pressure is 148.2 kPa at 21.1 °C [32–34]. There is a following equilibrium among ClF_3, ClF and F_2:

$$ClF_3 \leftrightarrow ClF + F_2$$

At room temperature, mainly ClF_3 is present in the system and the equilibrium moves to the right side with increase in temperature. Since the dissociation rates of ClF_3 are 1.75, 4.95, 11.95 and 50% at 250, 300, 350 and 460 °C, respectively, main species is ClF_3 except high temperatures. ClF_3 may decompose to atomic and radical species such as F, Cl and ClF_2 on the surface of carbon. These chemically active species would easily react with petroleum cokes, yielding gaseous compounds containing C, F, O and probably Cl. NF_3 is a stable compound at room temperature, but dissociates to atomic and radical species, i.e. F and NF_2 at high temperatures [35]. Fluorination of carbon by ClF_3 and NF_3 is therefore similar to radical reactions causing surface etching by atoms and radicals generated by the decomposition of ClF_3 and NF_3. This type reaction gives various fluorocarbon gases. This would be the reason why no surface fluorine was detected in the samples fluorinated by ClF_3 and NF_3 except only one case (PC fluorinated by NF_3 at 300 °C) while the large amounts of surface fluorine, 5.2–50.2 at.% were found in the case of the

Table 4
Composition of petroleum cokes (at.%) and those fluorinated by F_2

Fluorination temperature (°C)	PC			PC1860			PC2100			PC2300			PC2600			PC2800		
	C	F	O	C	F	O	C	F	O	C	F	O	C	F	O	C	F	O
Original	94.8	–	2.3	99.4	–	0.6	100	–	0	100	–	0	100	–	0	100	–	0
200	96.5	1.2	2.3	99.8	0	0.2	100	0	0	100	0	0	100	0	0	99.8	0	0.2
300	90.4	7.3	2.3	99.2	0.6	0.2	100	0.4	0	99.6	0.3	0.1	100	0.3	0	99.5	0.4	0.1

0 for F: within detection limit (<0.2 at.%). Original petroleum coke contained 2.9 at.% hydrogen. No hydrogen was detected in heat-treated petroleum cokes.

Table 5
Binding energies of C 1s, O 1s and F 1s electrons and surface composition of petroleum cokes and those fluorinated by F_2

Fluorination temperature	PC			PC1860			PC2100			PC2300			PC2600			PC2800		
	C	O	F	C	O	F	C	O	F	C	O	F	C	O	F	C	O	F
Original	284.3	531.7	–	284.3	531.7	–	284.3	531.9	–	284.3	531.7	–	284.3	531.8	–	284.3	531.9	–
300 °C	285.3	531.9	688.8	284.1	531.9	687.6	284.3	531.8	687.5	284.1	531.8	687.6	284.2	532.0	687.4	284.1	531.8	687.3
eV	290.1			288.6			288.6						288.3					
Original	87.8	12.2	–	91.7	8.3	–	92.3	7.7	–	92.4	7.6	–	91.1	8.9	–	93.4	6.6	–
300 °C (at.%)	44.8	5.0	50.2	72.7	4.9	22.4	75.9	6.3	17.8	81.8	6.5	11.7	83.3	6.6	10.1	89.2	5.6	5.2

Table 6
Surface concentrations (at.%) of F, Cl and N of petroleum cokes fluorinated by ClF_3 and NF_3

Sample	Fluorination temperature (°C)	ClF_3		NF_3	
		F	Cl	F	N
PC	200	0	1.0	0	0.5
	300	0	1.4	2.6	0.4
PC1860	200	0	0.6	0	0
	300	0	0.9	0	0
PC2300	200	0	1.1	0	0
	300	0	0.4	0	0
	400	0	0.5	0	0
	500	0	1.1	0	0
PC2800	200	0	1.1	0	0
	300	0	0.3	0	0
	400	0	0.7	0	0
	500	0	1.0	0	0

fluorination by F_2 as given in Table 5. This difference in the surface fluorine concentrations is attributed to the different reaction mechanisms between ClF_3/NF_3 and F_2. It is known that fluorination of organic compounds by elemental fluorine proceeds via electrophilic reaction, that is, $F^{\delta+}$ attacks $C^{\delta-}$ with higher electron density [36,37]. Theoretical calculation made for fluorination of nitrogen-substituted carbon, C_xN by elemental fluorine gave the same result [38]. This kind of reaction would give stable C–F bonds without breaking C–C bond of carbon, that is, yield solid product. Another interesting result is that small amounts of chlorine were detected in the samples fluorinated by ClF_3. Since ClF_3 has $Cl^{\delta+}$–$F^{\delta-}$ bond, $Cl^{\delta+}$ generated by the decomposition of ClF_3 would preferentially attack $C^{\delta-}$ of carbon, yielding C–Cl bond. This may be the reason why small amounts of chlorine were detected in the samples. When petroleum cokes were fluorinated by NF_3, only PC with low crystallinity contained small amounts of nitrogen probably bonded to edge of graphene layers. Nitrogen would be removed as N_2 gas from the reaction systems.

2.3. Electrochemical behavior of surface-fluorinated petroleum cokes in 1 mol/dm^3 $LiClO_4$–ethylene carbonate (EC)/diethyl carbonate (DEC)

Galvanostatic charge/discharge cycling was performed at current densities of 60 and 150 mA/g between 0 and 3 V relative to Li/Li^+ reference in 1 mol/dm^3 $LiClO_4$–ethylene carbonate (EC)/diethyl carbonate (DEC) at 25 °C. Since metallic lithium was used as a counter electrode, lithium deintercalation from graphite or carbon is a charging process. However, in this paper, it is called as a discharge process according to the naming in the practical secondary lithium battery.

Effect of surface fluorination was observed for heat-treated petroleum cokes. Fig. 5 shows charge/discharge curves obtained at 60 mA/g for PC2800 and that fluorinated by F_2 at 300 °C [11]. A large reduction current was observed between 1 and 0 V versus Li/Li^+ at 1st cycle in Fig. 5(a), indicating the electrochemical decomposition of EC and formation of SEI. This reduction current was highly reduced after surface

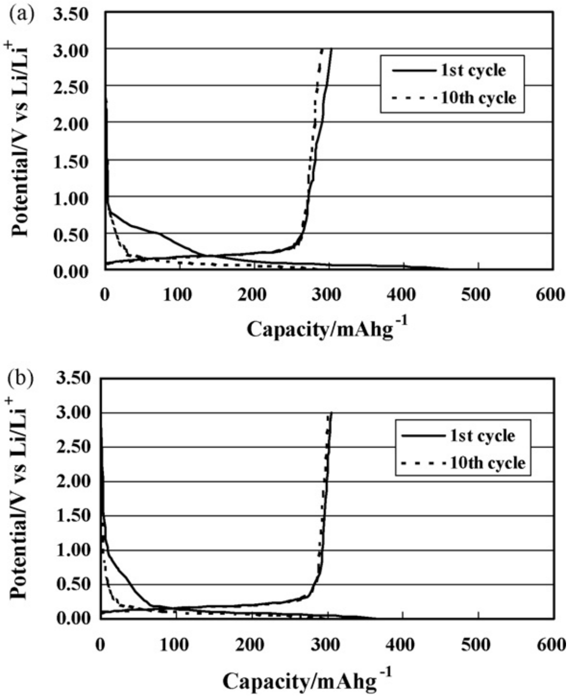

Fig. 5. Charge/discharge curves for PC2800 (a) and those fluorinated by F_2 at 300 °C (b), obtained at 60 mA/g in 1 mol/dm^3 $LiClO_4$–EC/DEC.

fluorination as shown in Fig. 5(b), which gave rise to the large increase in first coulombic efficiencies (decrease in irreversible capacities) of PC2800. It was also found that first discharge capacities for some fluorinated PC2600 and PC2800 samples were increased 23–42 mAh/g at 150 mA/g though no increase was observed at 60 mA/g. The most interesting results were obtained about first coulombic efficiencies as mentioned above. First coulombic efficiencies of PC, PC1860 and PC2100 fluorinated at 300 °C were lower than those of non-fluorinated samples. However, those of PC2300, PC2600 and PC2800 were increased by 12.1–18.2% at 60 mA/g and 13.3–25.8% at 150 mA/g when they were fluorinated at 300 °C, as given in Table 7 [11–13].

The increase in the first discharge capacities was mainly observed for many PC1860, PC2300 and PC2800 samples fluorinated by ClF_3 and NF_3 as given in Table 8 [26]. Surface fluorination increased the first discharge capacities by ~52 mAh/g (~24.0%) and ~63 mAh/g (~29.6%) at 150 mA/g for PC2300 and PC2800, respectively. In case of PC1860, first discharge capacities increased by ~25.3%. First discharge capacities were thus increased in most of fluorinated PC1860, PC2300 and PC2800 samples. The increase in first coulombic efficiencies (~10.1%) was also found for PC2800 with higher crystallinity than PC2300 and PC1860.

Structural factors should be considered for the increase in first coulombic efficiencies and first discharge capacities of graphitized petroleum cokes by fluorination. The change in the surface areas of PC1860, PC2300, PC2600 and PC2800 was small before and after fluorination by F_2 as given in Table 3. In case of the fluorination by ClF_3 and NF_3, BET surface areas of all petroleum coke samples were decreased. This result is an advantage for graphitized petroleum cokes because electrochemical decomposition of EC does not increase. Other advantages given by fluorination would be the increase in surface disorder and opening of closed edge of graphitized

Table 7
First coulombic efficiencies (%) for petroleum cokes fluorinated by F_2 in 1 mol/dm^3 $LiClO_4$–EC/DEC at 60 and 150 mA/g

Current density (mA/g)	Fluorination temperature (°C)	Petroleum coke					
		PC	PC1860	PC2100	PC2300	PC2600	PC2800
60	Original	72.3	90.2	90.5	71.9	67.0	65.4
	200	68.6	87.9	91.7	72.4	66.7	60.5
	300	47.4	83.3	87.1	84.1	79.1	83.6
150	Original	–	89.1	88.2	70.0	56.3	63.6
	200	–	88.0	89.8	76.5	60.3	59.6
	300	–	81.8	84.6	83.3	82.1	79.5

Table 8
First discharge capacities (mAh/g) and first coulombic efficiencies (%) for petroleum cokes fluorinated by ClF_3 and NF_3 in 1 mol/dm^3 $LiClO_4$–EC/DEC at 150 mA/g

Fluorinating agent	Fluorination temperature (°C)	PC1860		PC2300		PC2800	
		mAh/g	%	mAh/g	%	mAh/g	%
	Original	182	88.2	216	75.7	213	62.8
ClF_3	200	203	88.2	230	66.8	211	66.4
	300	228	83.6	240	79.0	201	67.2
	400	–	–	245	69.6	276	61.1
	500	–	–	256	73.8	250	72.9
NF_3	200	209	85.9	202	76.9	244	72.4
	300	225	86.2	241	78.5	247	72.2
	400	–	–	268	71.1	253	65.2
	500	–	–	259	73.6	266	65.0

petroleum cokes by carbon–carbon bond breaking. Closed edge plane would be destroyed and opened by fluorination reaction with formation of CF_2/CF_3 groups. The opening of edge planes and increase in the surface disorder can make easier the SEI formation and Li^+ ion intercalation into petroleum coke electrodes. The increase in the first coulombic efficiencies was the main results obtained for graphitized petroleum cokes fluorinated by F_2 while first discharge capacities were increased in many petroleum cokes fluorinated by ClF_3 and NF_3. The reaction of F_2 with a carbon material is an electrophilic reaction, giving a solid fluoride layers with high disorder. Graphitized petroleum cokes with high disorder increased first coulombic efficiencies with decomposition of less amounts of EC for the formation of SEI. On the other hand, the reactions of ClF_3 and NF_3 with carbon materials are surface etching by atomic and radical species generated by the decomposition of ClF_3 and NF_3, effectively destroying and removing the closed edge planes, which makes easy the Li^+ ion intercalation and deintercalation into and from petroleum cokes. First discharge capacities were therefore increased by the fluorination of graphitized petroleum cokes. The difference in the fluorination reactions between F_2 and ClF_3/NF_3 thus gives somewhat different effects to the charge/discharge characteristics of fluorinated petroleum cokes. Surface fluorine reacts with lithium in the charging process to give LiF, which increases the irreversible capacity. From this point of view, ClF_3 and NF_3 are the better fluorinating agents than F_2 because no surface fluorine was detected in the fluorinated samples except one case. However, it was recently found that surface fluorine was significantly lost during the electrode preparation [39]. The effect of surface fluorine is therefore almost negligible when F_2 is used as a fluorinating agent.

3. Conclusions

Effect of surface fluorination of petroleum coke samples on the anode performance of secondary lithium batteries is summarized. Surface structure change was found by TEM observation. High temperature treatment of petroleum coke gives round and closed edge planes by carbon–carbon bond formation at edge of graphene layers accompanying the elimination of surface oxygen. Formation of SEI and Li^+ ion intercalation are difficult on the surface of graphitized petroleum cokes with closed edge. Fluorination of a carbon material by F_2 is an electrophilic reaction, yielding solid fluorinated layers. Surface fluorination of PC2800 by F_2 destroyed the closed edge planes and increased surface disorder. On the other hand, the fluorination by ClF_3 and NF_3 is a radical reaction causing surface etching. Fluorination by ClF_3 and NF_3 effectively destroyed and opened the closed edge. No surface fluorine was detected except only one sample. Surface fluorination of graphitized petroleum cokes (PC2300, PC2600 and PC2800) by F_2 highly reduced the electrochemical decomposition of EC, i.e. increasing their first coulombic efficiencies by 12.1–18.2% at 60 mA/g and by 13.3–25.8% at 150 mA/g in 1 mol/dm^3 $LiClO_4$–EC/DEC. On the other hand, surface fluorination by ClF_3 and NF_3 increased the first discharge capacities of many PC1860, PC2300 and PC2800 samples by ~63 mAh/g (~29.5%) at 150 mA/g.

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