

Electrochemical behavior of surface-modified petroleum cokes in propylene carbonate containing solvents

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Abstract

Surface modification of petroleum coke (PC) and those heat-treated at 1860, 2300 and 2800 °C (PC1860, PC2300 and PC2800) has been performed by F₂, ClF₃ and NF₃ to improve their charge/discharge characteristics in propylene carbonate containing solvents. Surface fluorination by F₂ increased surface disorder of PC1860, PC2300 and PC2800, leading to increase in their first coulombic efficiencies in 1 mol dm⁻³ LiClO₄-ethylene carbonate (EC)/diethyl carbonate (DEC)/propylene carbonate (PPC) (1:1:1 in volume) solution. First coulombic efficiencies were the largest in fluorinated PC1860 with the highest surface disorder. However, surface modification by ClF₃ and NF₃ did not increase surface disorder of petroleum cokes, being not as effective as the fluorination with F₂ to increase first coulombic efficiencies of petroleum cokes. The reactions of ClF₃ and NF₃ with carbon materials are radical reactions while the reaction with F₂ is an electrophilic reaction yielding fluorinated layers with high disorder. Surface modification using F₂, ClF₃ and NF₃ also increased first charge capacities of PC and PC1860.

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1. Introduction

Since the commercialization of lithium ion battery in 1991, secondary lithium battery is now widely used as electric power sources for many kinds of electric devices such as portable phones, personal computers and so on [1]. Since cathode material is lithium-containing transition metal oxide, anode should have a small irreversible capacity, that is, high first coulombic efficiency. If not, the utilization of oxide cathode is largely reduced. For this reason, mixtures of natural and synthetic graphites are mainly used as anodes because of their small irreversible capacities (high first coulombic efficiencies). Synthetic graphite is prepared by heat-treatment of a graphitizing (graphitizable) carbon at 2800–3000 °C. The crystallinity of synthetic graphite is normally somewhat lower than that of natu-

ral graphite. Therefore, reversible capacity of synthetic graphite is slightly lower than that of natural graphite. Organic solvent consists of two components, that is, a high dielectric solvent such as ethylene carbonate (EC), propylene carbonate (abbreviated to PPC to distinguish from petroleum coke (PC)), etc. and a low viscosity solvent such as dimethyl carbonate (DMC), methyl ethyl carbonate (MEC), diethyl carbonate (DEC), etc. For high crystalline graphite, EC-containing solvent should be used for the formation of surface film (Solid Electrolyte Interphase or Interface, SEI) with electrochemical decomposition of a small amount of solvent. PPC cannot be used for graphite anode because electrochemical reduction continues without quick formation of SEI, but can be used for a low crystalline carbon. Surface disorder of high crystalline graphite is normally lower than that of low crystalline carbon. Molecular size of PPC is larger than that of EC. It means that the size of Li⁺ ion solvated by PPC molecules is larger than the size of Li⁺ ion solvated by EC. This may be the reason why EC should be used for graphite with low surface disorder. Surface structures

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may be different between natural and synthetic graphites. Natural graphite powder is prepared by pulverizing a block or flake graphite and sieving graphite powder mixtures with different particle sizes. Therefore, the surface of natural graphite powder is opened though some carbon atoms may be terminated by oxygen species. On the other hand, synthetic graphite is prepared by high temperature treatment of a graphitizing carbon. It has been found from the recent studies that surface edge planes of petroleum coke containing a small amount of oxygen is closed by carbon–carbon bond formation during the heat-treatment at high temperatures [2–5]. The closure of edge planes significantly reduced first coulombic efficiencies of graphitized petroleum cokes [2–5]. Since the electrochemical redox reactions take place on the surface of solid electrode, surface structure, in particular, edge structure of carbonaceous anode gives significant effects to electrochemical characteristics because Li^+ ion is inserted from edge planes. In order to improve the electrochemical properties of carbonaceous anodes, some methods of surface modification have been attempted [1,6–9]. They are surface fluorination [1–5,10–16], surface oxidation [17–24], metal or metal oxide coating [25–29], carbon coating [30–38], and polymer or Si coating [39–45]. Many kinds of composite electrodes with oxide, metal(s) or Si have been also fabricated and examined [46–68]. Surface modification gives positive effects to carbonaceous anodes regarding reversible capacities, first coulombic efficiencies (irreversible capacities), cycleability and so on.

Surface fluorination with elemental fluorine (F_2) and plasma-treatment using CF_4 gas has been applied to high crystalline natural graphite powder samples with different particle sizes (average particle sizes: 7, 25 and 40 μm and BET surface areas: 4.79, 3.71 and 2.94 $\text{m}^2 \text{g}^{-1}$) [1,10–16]. Since fluorination using F_2 is a strong oxidation reaction, surface modification with F_2 was performed under mild conditions. Surface fluorination with F_2 gas and plasma-treatment increased BET surface areas and small meso-pores with diameters of 1.5–2 and 2–3 nm. Surface disorder evaluated by Raman spectroscopy was also increased. Charge/discharge cycling tests demonstrated significant increase in discharge capacities without decrease in first coulombic efficiencies. High discharge capacities of 380–390 mAh g^{-1} exceeding the theoretical capacity of graphite, 372 mAh g^{-1} was obtained in 1 mol dm^{-3} $\text{LiClO}_4\text{-EC/DEC}$ at a current density of 60 mA g^{-1} . Surface fluorination of natural graphite powder samples (average particle sizes: 5, 10 and 15 μm and BET surface areas: 12.1, 7.2 and 5.3 $\text{m}^2 \text{g}^{-1}$) with ClF_3 highly reduced the electrochemical decomposition of PPC, that is, increased first coulombic efficiencies in PPC-containing solvent. Surface fluorination of heat-treated petroleum cokes with F_2 destroyed and opened the closed edge planes, highly increasing first coulombic efficiencies of petroleum cokes heat-treated at 2300–2800 $^\circ\text{C}$ in 1 mol dm^{-3} $\text{LiClO}_4\text{-EC/DEC}$ [2–4]. Fluorination of the same petroleum coke samples with ClF_3 and NF_3 gases effectively destroyed the closed edge planes by radical reactions, increasing first charge capacities (Li^+ deintercalation from petroleum cokes) in the same EC containing solvent [5]. It is known that PPC is not a suitable solvent for graphite anodes because of its continuous decomposition without formation of SEI. If PPC can

be used for graphitic materials, it is much more convenient for the practical application. In the present study, electrochemical behavior of petroleum cokes surface-fluorinated by F_2 , ClF_3 and NF_3 has been investigated using PPC containing solvent.

2. Experimental

2.1. Surface fluorination and analyses of petroleum coke samples

Carbon materials used in the present study were petroleum coke and those heat-treated at 1860, 2300 and 2800 $^\circ\text{C}$ (PC1860, PC2300 and PC2800). Their interlayer spacings of (002) diffraction lines were 0.3450, 0.3385, 0.3366 and 0.3361 nm for PC, PC1860, PC2300 and PC2800, respectively, being larger than that of high crystalline natural graphite (0.3354 nm). This means that these petroleum cokes have the lower crystallinity than natural graphite.

The result of elemental analysis of C and H suggested that PC and PC1860 contained small amounts of oxygen (C: 94.8, H: 2.9 (O: 2.3) at.% for PC; C: 99.4 (O: 0.6) at.% for PC1860; C: 100 at.% for PC2300 and PC2800) [2,5]. The existence of surface oxygen was shown by X-ray photoelectron spectroscopy (XPS) [2,5]. Surface fluorination was made by F_2 (3×10^4 Pa) at 200 $^\circ\text{C}$ and 300 $^\circ\text{C}$ for 2 min, and by ClF_3 and NF_3 (3×10^4 Pa) at 200–500 $^\circ\text{C}$ for 2 min, using a nickel reactor. Surface composition of fluorinated samples was determined by XPS [2,5]. Surface areas were measured by BET method using nitrogen [2,5], and surface disorder was evaluated by Raman spectroscopy. Surface structure change was also investigated by transmission electron microscopy (TEM).

2.2. Electrochemical measurements of surface-fluorinated petroleum coke samples

Three electrode-cell with petroleum coke sample as a working electrode and metallic lithium as counter and reference electrodes was used for galvanostatic charge/discharge experiments. Electrolyte solution was 1 mol dm^{-3} $\text{LiClO}_4\text{-EC/DEC/PPC}$ (1:1:1 in volume). Petroleum coke electrode was prepared as follows. Petroleum coke sample was dispersed in *N*-methyl-2-pyrrolidone (NMP) containing 12 wt.% poly(vinylidene fluoride) (PVdF) and pasted on a foamed nickel or copper plate. The electrode was dried at 120 $^\circ\text{C}$ under vacuum overnight. In case of a foamed nickel, the electrode was pressed before electrochemical measurement. Charge/discharge experiments were performed at current densities of 60 and 150 mA g^{-1} between 0 and 3 V relative to Li/Li^+ in a glove box filled with Ar at 25 $^\circ\text{C}$.

3. Results and discussion

3.1. Surface structure changes of petroleum coke samples by fluorination

The fluorination mechanisms of carbon materials are different between F_2 and ClF_3/NF_3 as already reported [5,16]. Fluorination of a carbon material by F_2 is an electrophilic

Table 1
Surface composition (at.%) of petroleum coke samples (data for F₂: [2,3]; data for ClF₃ and NF₃: [5])

Petroleum coke	Fluorination temperature	F ₂			ClF ₃				NF ₃			
		C	O	F	C	O	F	Cl	C	O	F	N
PC	Original	87.8	12.2	–	87.8	12.2	–	–	87.8	12.2	–	–
	200 °C	–	–	–	88.1	10.9	0.0	1.0	88.2	11.3	0.0	0.5
	300 °C	44.8	5.0	50.2	88.0	10.6	0.0	1.4	85.8	11.2	2.3	0.4
PC1860	Original	91.7	8.3	–	91.7	8.3	–	–	91.7	8.3	–	–
	200 °C	–	–	–	91.2	8.2	0.0	0.6	92.1	8.8	0.0	0.0
	300 °C	72.7	4.9	22.4	90.8	8.3	0.0	0.9	92.4	7.6	0.0	0.0
PC2300	Original	92.4	7.6	–	92.4	7.6	–	–	92.4	7.6	–	–
	200 °C	–	–	–	93.1	5.8	0.0	1.1	92.3	7.7	0.0	0.0
	300 °C	81.8	6.5	11.7	93.4	6.2	0.0	0.4	91.2	8.8	0.0	0.0
	400 °C	–	–	–	92.2	7.3	0.0	0.5	94.1	5.9	0.0	0.0
	500 °C	–	–	–	89.7	9.2	0.0	1.1	94.2	5.8	0.0	0.0
PC2800	Original	93.4	6.6	–	93.4	6.6	–	–	93.4	6.6	–	–
	200 °C	–	–	–	93.1	5.8	0.0	1.1	93.3	6.7	0.0	0.0
	300 °C	89.2	5.6	5.2	94.4	5.3	0.0	0.3	91.8	8.2	0.0	0.0
	400 °C	–	–	–	93.4	5.9	0.0	0.7	95.5	4.5	0.0	0.0
	500 °C	–	–	–	92.6	6.4	0.0	1.0	94.7	5.3	0.0	0.0

reaction where F^{δ+} preferentially attacks C^{δ-} with a high electron density, yielding covalently bonded C–F layers. Surface fluorine was always detected as given in Table 1 [2,3]. Fluorine concentration decreased with increasing heat-treatment temperature of petroleum coke because the reactivity of graphitized petroleum coke with F₂ was diminished by closure of surface edge planes caused by carbon–carbon bond formation during the graphitization process [2–4]. On the other hand, high temperature fluorination reactions of a carbon material with ClF₃ and NF₃ are radical reactions by F, Cl, ClF₂, NF₂, etc., which are generated by thermal decomposition of ClF₃ and NF₃ [5,16]. Therefore, the fluorination reactions by ClF₃ and NF₃ have surface etching effect and main products are fluorine containing gaseous compounds such as CF₄, COF₂ and so on. Surface analysis indicated that no fluorine was detected except only one sample (PC fluorinated by NF₃ at 300 °C) while trace amounts of chlorine were found for all samples fluorinated by ClF₃ as given in Table 1 [5]. Since ClF₃ has a Cl^{δ+}–F^{δ-} bond, Cl^{δ+} may preferentially attack C^{δ-} of graphene layers, forming C–Cl bond. Surface areas of fluorinated samples are different depending on the fluorinating agents as given in Table 2 [2,3,5].

Table 2
Surface areas (m² g⁻¹) of petroleum coke samples (data for F₂: [2,3]; data for ClF₃ and NF₃: [5])

Fluorination gas	Fluorination temperature	Petroleum coke			
		PC	PC1860	PC2300	PC2800
F ₂	Original	5.99	3.11	2.19	2.36
	200 °C	8.06	3.31	2.27	2.73
	300 °C	25.2	3.20	2.25	2.81
ClF ₃	200 °C	4.57	2.32	2.07	1.84
	300 °C	4.21	2.46	2.12	1.88
NF ₃	200 °C	4.48	2.54	1.89	1.43
	300 °C	4.00	2.53	1.74	1.25

When petroleum cokes were fluorinated by F₂, surface areas were increased or nearly the same as those of non-fluorinated samples. However, when ClF₃ and NF₃ were used, surface areas were clearly reduced by surface etching effect due to atomic and radical species generated by thermal decomposition of ClF₃ and NF₃. Peak intensity ratio of D-band to G-band (*I_D/I_G*) in Raman spectrum qualitatively shows the level of surface disordering of a carbon material. *R* (= *I_D/I_G*) values calculated by peak intensity ratios of Raman spectra coincide well with the reaction mechanisms of F₂ and ClF₃/NF₃ with carbon materials and the data given in Tables 1 and 2. *R* values of petroleum cokes, in particular, heat-treated petroleum cokes were increased by fluorination with F₂ as given in Table 3 because fluorinated layers with covalent C–F bonds were formed in surface region [3]. *R*-value was the largest in PC1860 among three heat-treated petroleum cokes, which indicates that the degree of surface disorder was the highest in PC1860. PC had a large *R*-value after fluorination due to the formation of thick fluorinated layers. On the other hand, *R*-values were not changed by the fluorination

Table 3
R (= *I_D/I_G*) values of petroleum coke samples, obtained from peak intensity ratios of Raman spectra (data for F₂: [3])

Fluorination gas	Fluorination temperature	Petroleum coke			
		PC	PC1860	PC2300	PC2800
F ₂	Original	0.87	0.49	0.21	0.18
	300 °C	0.94	0.78	0.68	0.43
	ClF ₃	200 °C	0.93	0.51	0.29
ClF ₃	300 °C	0.93	0.49	0.26	0.16
	400 °C	–	–	0.27	0.15
	500 °C	–	–	0.26	0.16
NF ₃	200 °C	0.93	0.51	0.26	0.16
	300 °C	0.78	0.50	0.26	0.16
	400 °C	–	–	0.25	0.16
	500 °C	–	–	0.25	0.15

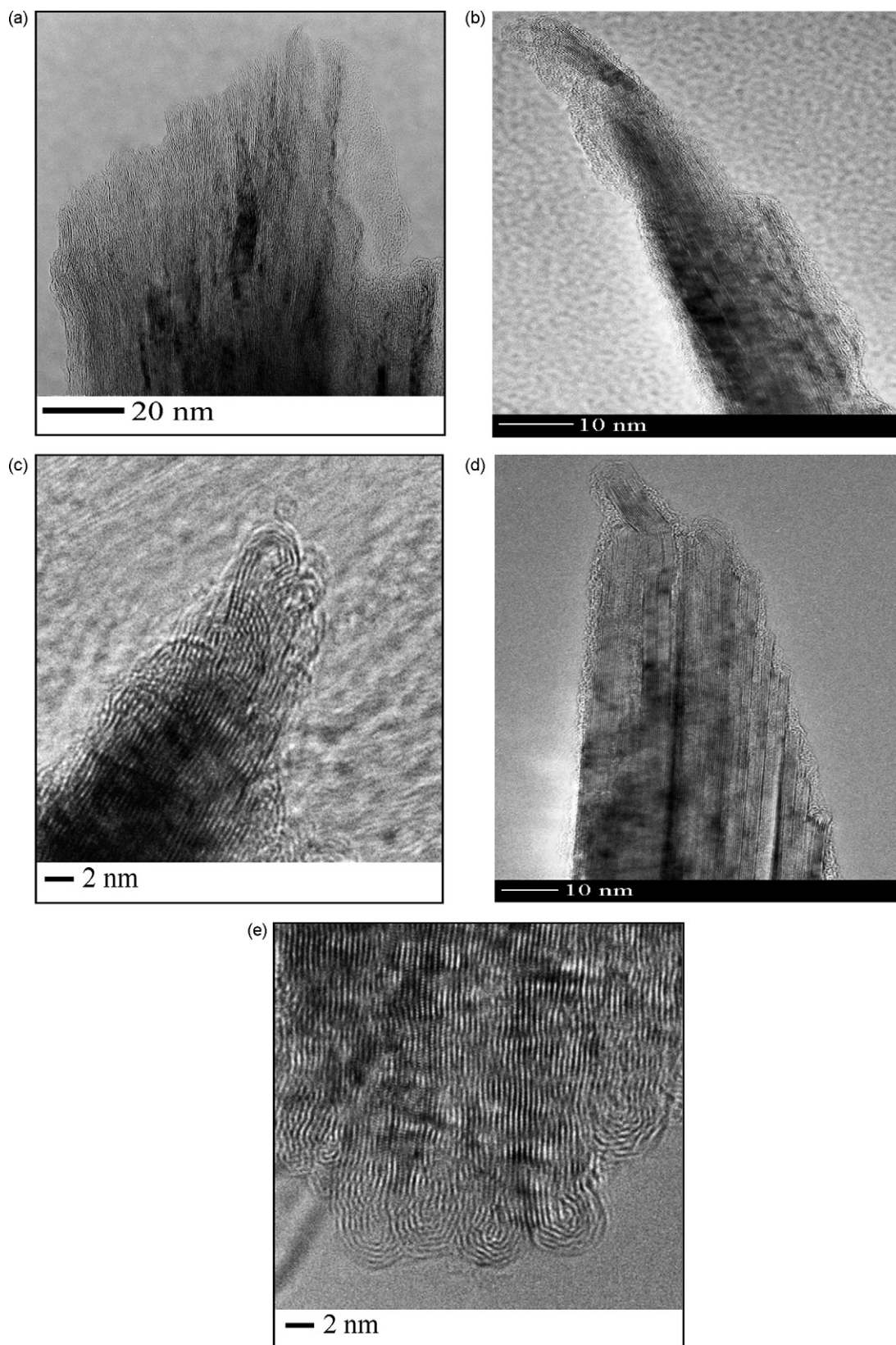


Fig. 1. TEM images of PC2800 fluorinated by F_2 : (a) and (b), ClF_3 : (c) and NF_3 : (d) and (e) at 400 °C.

Table 4
First charge capacities (mAh g⁻¹) and first coulombic efficiencies (%) of petroleum coke samples, obtained at 60 mA g⁻¹

Fluorination gas	Fluorination temperature	PC		PC1860		PC2300		PC2800	
		mAh g ⁻¹	%	mAh g ⁻¹	%	mAh g ⁻¹	%	mAh g ⁻¹	%
	Original	216	71.0	225	69.9	306	58.5	337	48.7
F ₂	200 °C	230	44.1	246	86.7	315	67.2	323	56.6
	300 °C	246	59.6	240	87.8	303	68.8	307	58.0
ClF ₃	200 °C	262	72.9	262	70.3	315	58.6	340	53.5
	300 °C	261	72.9	251	70.7	331	58.1	329	54.4
	400 °C	–	–	–	–	333	57.4	345	51.2
	500 °C	–	–	–	–	309	61.2	309	55.1
NF ₃	200 °C	240	73.1	250	75.7	319	60.1	334	55.5
	300 °C	247	73.4	252	74.2	324	57.2	323	54.9
	400 °C	–	–	–	–	315	54.8	323	50.2
	500 °C	–	–	–	–	335	56.2	344	52.8

with ClF₃ and NF₃. Transmission electron microscopic images of surface-fluorinated samples show surface structure changes by fluorination as shown in Fig. 1. It was already shown that edge planes of PC2800 are closed by carbon–carbon bond formation during heat-treatment at high temperatures [4]. The closure of edge planes hinders quick formation of SEI and Li⁺ insertion, reducing first coulombic efficiencies of PC2300, PC2600 and PC2800 [2–4]. Tables 1–3 indicate that surface region is more highly fluorinated and disordered in petroleum cokes fluorinated by F₂ than those treated by ClF₃ and NF₃. In consistency with the data in Tables 1–3, highly fluorinated and disordered surfaces are seen in PC2800 fluorinated by F₂. Thickness of the fluorinated layers with disorder is larger in Fig. 1a and b than in Fig. 1c–e. Closed edge planes are still observed in highly magnified images of PC2800 fluorinated by ClF₃ and NF₃ (Fig. 1c and e), however, the intensity of the images is low at the top of closed edge planes, which suggests that graphene layers are broken in many parts of surface by the etching effect with atomic and radical species formed by the decomposition of ClF₃ and NF₃.

3.2. Charge/discharge behavior of petroleum coke samples

Electrochemical properties of both non-fluorinated and fluorinated petroleum coke samples are different from those obtained in 1 mol dm⁻³ LiClO₄–EC/DEC [2–4]. First coulombic efficiencies for non-fluorinated samples decreased with increasing heat-treatment temperature of petroleum coke at current densities of both 60 and 150 mA g⁻¹ as given in Tables 4 and 5. This is consistent with a general trend that a low crystalline carbon is suitable for the use in PPC containing solvent. On the other hand, first charge capacities of non-fluorinated samples increased with increasing heat-treatment temperature of petroleum coke, i.e. with increasing crystallinity of petroleum coke in the similar manner to that observed in EC/DEC solution [2–4]. It has been found that effect of surface modification is different depending on the fluorinating agents, i.e. F₂ and ClF₃/NF₃. Figs. 2 and 3 show first charge/discharge potential curves obtained at 60 mA g⁻¹ for PC and PC1860 samples fluorinated by F₂, ClF₃ and NF₃, respectively. Fig. 4 exhibits those obtained at 60 mA g⁻¹ for PC2300 and PC2800 fluorinated by

Table 5
First charge capacities (mAh g⁻¹) and first coulombic efficiencies (%) of petroleum coke samples, obtained at 150 mA g⁻¹

Fluorination gas	Fluorination temperature	PC		PC1860		PC2300		PC2800	
		mAh g ⁻¹	%	mAh g ⁻¹	%	mAh g ⁻¹	%	mAh g ⁻¹	%
	Original	182	68.1	218	61.5	244	51.6	257	43.1
F ₂	200 °C	194	42.7	187	72.6	232	56.7	260	49.4
	300 °C	209	56.7	210	83.6	230	58.2	260	50.7
ClF ₃	200 °C	216	70.1	202	67.4	235	48.5	240	46.4
	300 °C	225	69.7	220	64.9	238	48.8	233	45.8
	400 °C	–	–	–	–	245	49.5	263	46.0
	500 °C	–	–	–	–	251	49.4	246	47.9
NF ₃	200 °C	205	70.5	232	70.5	231	50.1	238	48.1
	300 °C	206	69.7	212	69.2	227	50.2	240	48.0
	400 °C	–	–	–	–	253	51.0	246	47.5
	500 °C	–	–	–	–	273	50.8	250	50.2

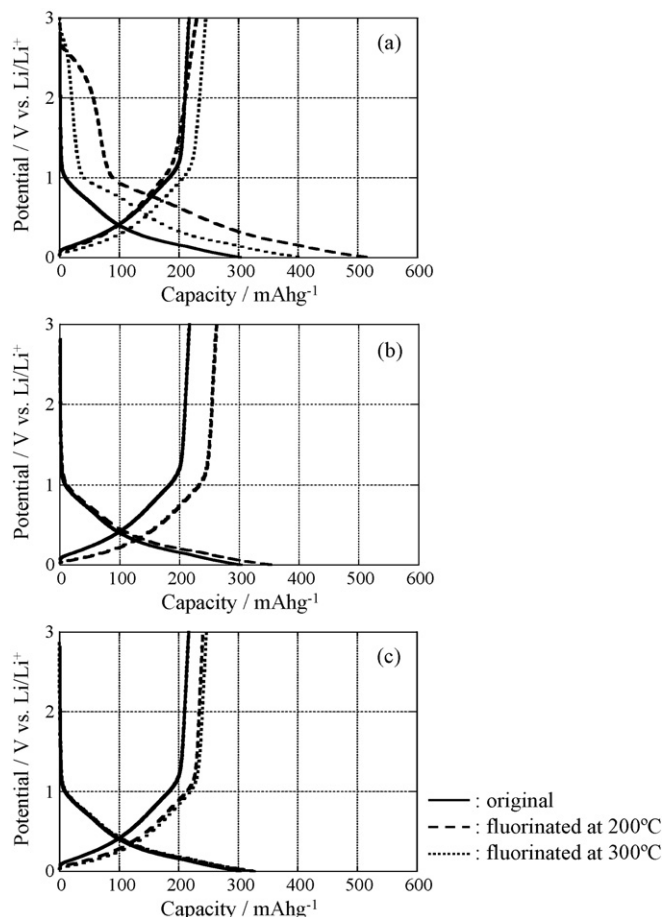


Fig. 2. First charge/discharge curves of PC fluorinated by F₂ (a), ClF₃ (b) and NF₃ (c), obtained at 60 mA g⁻¹.

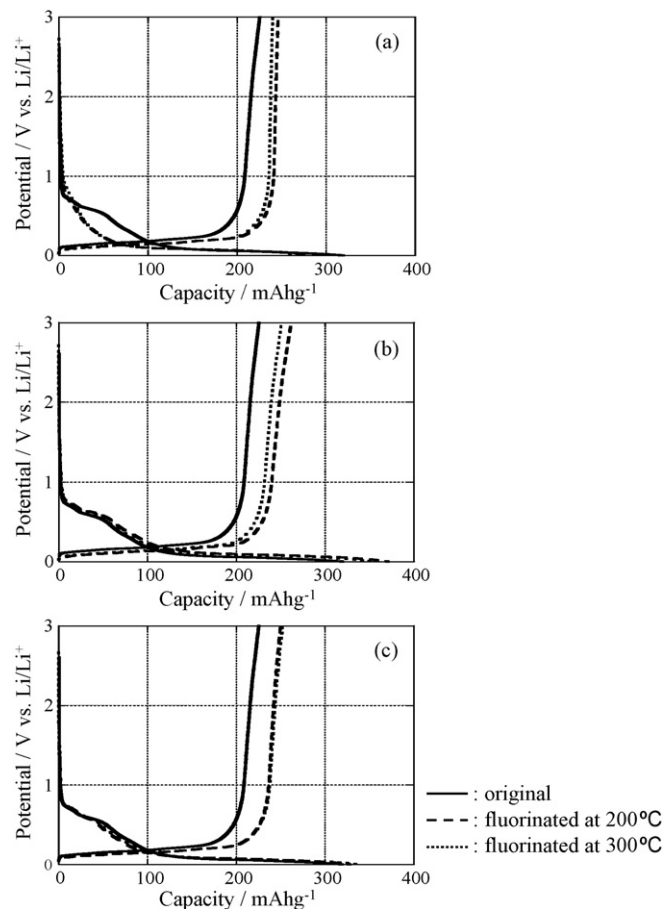


Fig. 3. First charge/discharge curves of PC1860 fluorinated by F₂ (a), ClF₃ (b) and NF₃ (c), obtained at 60 mA g⁻¹.

F₂. PC samples highly fluorinated by F₂ gave the higher charging potentials than non-fluorinated PC probably due to formation of LiF. However, surface fluorination of heat-treated petroleum cokes (PC1860, PC2300 and PC2800) by F₂ reduced the decomposition of PPC (Figs. 3a and 4), which led to the increase in first coulombic efficiencies. The increase in first coulombic efficiencies was in the range of 9.3–17.9% and 6.6–22.1% at 60 and 150 mA g⁻¹, respectively, as given in Tables 4 and 5. When the same surface-fluorinated petroleum cokes were examined in 1 mol dm⁻³ LiClO₄-EC/DEC, first coulombic efficiencies of petroleum cokes heat-treated between 2300 and 2800 °C were highly increased, while first coulombic efficiencies for those heat-treated at 1860 and 2100 °C were not changed [2–4]. Influence of surface fluorination on first coulombic efficiency is thus different depending on the organic solvents. As already known, a carbon with high disorder is suitable for PPC containing solvents. Table 3 shows that *R* value of PC1860 was larger than those of PC2300 and PC2800 before and after fluorination by F₂, indicating that surface disorder was higher in PC1860 than PC2300 and PC2800. In other words, not only first coulombic efficiencies themselves but also their increments by surface fluorination with F₂ were the largest in PC1860. Thus, PC1860 gave the best result regarding the improvement of first coulombic efficiencies by surface fluorination. PC had a large *R* value of

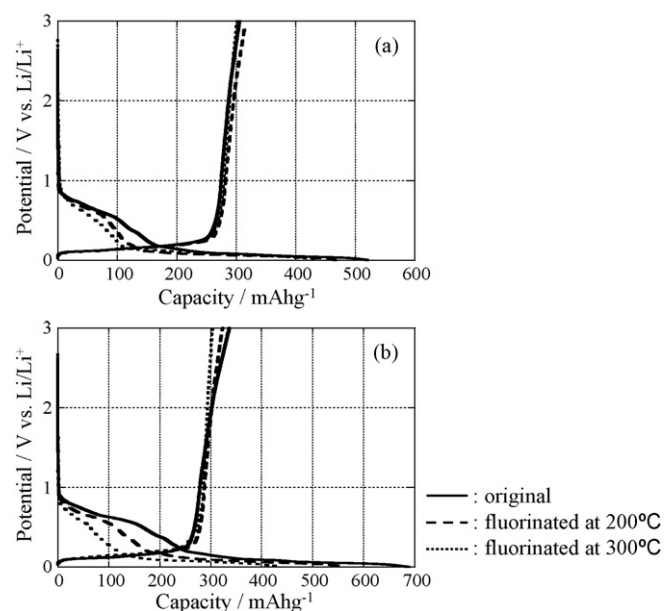


Fig. 4. First charge/discharge curves of PC2300 (a) and PC2800 (b) fluorinated by F₂, obtained at 60 mA g⁻¹.

0.94. However, this is due to the formation of a large amount of fluorinated layers as given in Table 1. Therefore, first coulombic efficiencies of surface-fluorinated PC samples were low because of the formation of LiF. On the other hand, the effect of surface modification with ClF_3 and NF_3 on first coulombic efficiency was small, though those of PC2800 and PC1860 were slightly increased ($\sim 9.0\%$). As already discussed, fluorination of carbon materials with ClF_3 and NF_3 did not increase the surface disorder of petroleum coke samples because of their radical reactions by atomic and radical species such as F, Cl, ClF_2 , NF_2 , etc. This may be the main reason why surface modification with ClF_3 and NF_3 is not effective for reducing the decomposition of PPC. Effect of surface fluorination was also found for first charge capacities of PC and PC1860 having relatively higher first coulombic efficiencies as shown in Figs. 2 and 3, and Tables 4 and 5. Increase in first charge capacities by surface fluorination was in the range of $14\text{--}46\text{ mAh g}^{-1}$ for PC and PC1860 samples at 60 mA g^{-1} and $12\text{--}43\text{ mAh g}^{-1}$ for PC at 150 mA g^{-1} . It was reported in a previous paper based on the impedance measurements that increase in first charge capacities of petroleum cokes heat-treated at 2100 and $2600\text{ }^\circ\text{C}$ by surface fluorination was related to decrease in their charge transfer resistances [4]. The resistances of SEI increased in all fluorinated samples, however, charge transfer resistances decreased in the petroleum cokes fluorinated at 200 and $300\text{ }^\circ\text{C}$. First charge capacities of the fluorinated samples increased by $19\text{--}42\text{ mAh g}^{-1}$ [4]. These results suggest that the increase in first charge capacities of PC and PC1860 was caused by reduction of charge transfer resistances by surface modification. Surface fluorine and chlorine atoms may react with deposited lithium on carbon electrode, giving LiF and LiCl. The formation of such halides may facilitate SEI formation though it reduces first coulombic efficiency. First coulombic efficiencies of PC fluorinated by F_2 were lower than those of other PC samples treated by ClF_3 and NF_3 . This may be because the surface fluorine reacted with lithium to give LiF. However, no surface fluorine was found in the samples treated by ClF_3 and NF_3 except one sample as given in Table 1. This is an advantage of surface modification using ClF_3 and NF_3 .

4. Conclusions

Heat-treatment of oxygen-containing petroleum coke at a high temperature ($\sim 2800\text{ }^\circ\text{C}$) gives rise to closure of edge planes by C–C bond formation [2–5]. To improve charge/discharge characteristics in propylene carbonate containing solvents, surface modification of petroleum coke and those heat-treated at 1860 , 2300 and $2800\text{ }^\circ\text{C}$ (PC1860, PC2300 and PC2800) has been performed by F_2 , ClF_3 and NF_3 . Fluorination of carbon materials by F_2 is an electrophilic reaction, yielding fluorinated graphene layers with high disorder while reactions of ClF_3 and NF_3 are radical reactions, giving surface etching effect by atomic and radical species generated by the decomposition of ClF_3 and NF_3 . No surface fluorine was detected when ClF_3 and NF_3 were used except only PC treated by NF_3 at $300\text{ }^\circ\text{C}$ while small amounts of chlorine were found in all samples modified by ClF_3 because $\text{Cl}^{\delta+}$ preferentially attacks carbon atom with higher electron density ($\text{C}^{\delta-}$), forming C–Cl bond. TEM

observation demonstrated surface structure changes of PC2800 by F_2 , ClF_3 and NF_3 . Surface fluorination by F_2 increased first coulombic efficiencies of PC1860, PC2300 and PC2800, being effective particularly for PC1860 with the higher surface disorder than PC2300 and PC2800. The increase in their first coulombic efficiencies was in the range of $9.3\text{--}17.9\%$ and $6.6\text{--}22.1\%$ at 60 and 150 mA g^{-1} , respectively. However, the effect of surface modification with ClF_3 and NF_3 was small, though first coulombic efficiencies of PC2800 and PC1860 were slightly increased ($\sim 9.0\%$). Effect of surface fluorination was also found for first charge capacities of PC and PC1860 having relatively higher first coulombic efficiencies. Increase in first charge capacities by surface fluorination was in the range of $14\text{--}46\text{ mAh g}^{-1}$ for PC and PC1860 samples at 60 mA g^{-1} and $12\text{--}43\text{ mAh g}^{-1}$ for PC at 150 mA g^{-1} . Effect of surface fluorination on the charge/discharge behavior of petroleum cokes was mainly observed for PC1860 and PC with high surface disorder.

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