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Surface structure and electrochemical characteristics of plasma-fluorinated petroleum cokes for lithium ion battery

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Abstract

Plasma-fluorination of petroleum coke and those heat-treated at 1860, 2300 and 2800 °C (abbreviated to PC, PC1860, PC2300 and PC2800) was conducted for 15, 30 and 60 min using CF₄ gas at 90 °C. Fluorine contents obtained by elemental analysis were negligible except PC fluorinated for 60 min (0.7 at.%). Fluorine concentration on the surface decreased with increasing heat-treatment temperature of petroleum coke, i.e. from PC to PC2800 when plasma-fluorination was made for 30 and 60 min. Transmission electron microscopic observation revealed that the closed edges of PC2800 were destroyed and opened by plasma-treatment. Plasma-fluorination increased surface disorder of heat-treated petroleum cokes, however, slightly reduced surface areas. These surface structure changes increased first coulombic efficiencies of PC2300 and PC2800 by 6–8 and 8–10% at both 60 and 150 mA g⁻¹, respectively.

Keywords: Plasma-fluorination; Surface modification; Carbon anode; Lithium ion battery

1. Introduction

Graphite is mainly used as anode of lithium ion battery because of its low potential, high coulombic efficiency (low irreversible capacity) and constant reversible capacity. Surface structure is one of the important factors influencing the electrode characteristics of carbonaceous anodes. Since carbon material has an anisotropic layered structure, surface edge structure and surface chemical species would give large effects to the electrode performance. Some methods of surface modification have been applied to carbon anode materials to improve their anode characteristics [1–5]. They include carbon coating [6–14], metal or metal oxide coating [15–21], surface oxidation [22–29], surface fluorination [30–40] and polymer or Si coating [41–47]. Carbon coating is a good method to improve electrode performance, in particular to reduce irreversible capacities [6–14].

Mild oxidation increases the capacities in some cases, however, strong oxidation degrades carbon materials [22–29]. Surface fluorination is effective for improving electrode characteristics of graphitic materials [30–40]. Light fluorination of natural graphite samples (average diameter: 7, 25 and 40 μm; BET surface area: 4.8, 3.4 and 2.7 m² g⁻¹) by F₂ gave the higher capacities of 380–390 mAh g⁻¹ than the theoretical value of graphite, 372 mAh g⁻¹ at 60 mA g⁻¹ [30–35]. Surface fluorination of graphitized petroleum cokes by F₂ and ClF₃/NF₃ highly increased their first coulombic efficiencies and first charge capacities, respectively [37–39].

Natural graphite powder is prepared by pulverization of block or flake graphite and sieving of pulverized mixtures with various particle sizes. The edge surface of powdery natural graphite is therefore opened though some carbon atoms may be terminated by oxygen. On the other hand, synthetic graphite is prepared by heat-treatment of a graphitizing carbon at high temperatures such as 2800–3000 °C. Surface edge structure can be therefore modified during the graphitization process. It was recently reported that surface structure of oxygen containing

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carbon changed during the heat-treatment at high temperatures. Surface-oxidized carbon fiber gave closed edge plane by the heat-treatment at 3000 °C [48]. Petroleum coke is one of good examples as a starting carbon for preparing synthetic graphite. Heat-treatment of oxygen containing petroleum coke at 2800 °C also gave rise to the closed edge plane by carbon–carbon bond formation [39,40]. The closure of edge surface was confirmed by transmission electron microscopic observation [39,40]. Since heat-treatment of a graphitizing carbon is made in a reduced atmosphere, surface oxygen would be eliminated as CO, accompanying carbon–carbon bond breaking. Graphene layers are connected with each other at the edge by the recombination of bare carbon atoms, giving the closed edge plane with round shape. Electrochemical reduction of a solvent and subsequent formation of surface film (solid electrolyte interphase or interface: SEI) may be difficult on such closed edge plane. The SEI formation probably needs the decomposition of a large amount of a solvent such as ethylene carbonate (EC). In fact, first coulombic efficiencies of petroleum cokes heat-treated at 1860–2800 °C decreased with increasing heat-treatment temperature [37–39]. This is attributed to the effect of closure of edge plane by carbon–carbon bond formation. Light fluorination of graphitized petroleum cokes by F₂ destroyed and opened the closed edge plane, increasing their first coulombic efficiencies, i.e. reducing the irreversible capacities [37–39]. On the other hand, fluorination of petroleum cokes by ClF₃ and NF₃ gave quite different results from those obtained by the fluorination using F₂ [40]. Main effect obtained by the fluorination with ClF₃ and NF₃ was increase in first charge capacities of heat-treated petroleum cokes [40]. It was found that the fluorination reactions of carbon materials with ClF₃ and NF₃ are radical reactions while the fluorination with F₂ is an electrophilic reaction, yielding surface fluorinated layers with high disorder. In the present study, we have applied plasma-fluorination technique to the surface modification of petroleum cokes as examples of synthetic graphites and evaluated the effect of plasma-treatment on their electrode characteristics in comparison with the results previously obtained by the fluorination with F₂ and ClF₃/NF₃.

2. Experimental

2.1. Plasma-fluorination and analyses of petroleum cokes

Petroleum coke and those heat-treated at 1860, 2300 and 2800 °C (abbreviated to PC, PC1860, PC2300 and PC2800) were used as starting carbon materials. The interlayer spacings of their (0 0 2) diffraction lines were 0.3450, 0.3385, 0.3366 and 0.3361 nm for PC, PC1860, PC2300 and PC2800, respectively [37–40]. Petroleum coke sample was placed in the center of the chamber on the electrode connected to rf. Plasma-fluorination of these petroleum coke samples was made using CF₄ gas under the following conditions: CF₄ flow rate, 8 cm³ min^{−1}; total gas pressure, 5.0 Pa; power, 80 W; plasma frequency, 13.56 MHz; sample temperature, 90 °C and plasma-treatment time, 15, 30 and 60 min. The *d*(0 0 2) values of petroleum cokes were nearly the same before and after the plasma-fluorination. The composi-

tion and surface structure change were investigated by elemental analysis, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Raman spectroscopy and BET surface area measurements using nitrogen gas.

2.2. Electrochemical measurements of plasma-fluorinated petroleum cokes

Electrochemical characteristics of plasma-fluorinated petroleum coke samples were evaluated by cyclic voltammetry and galvanostatic charge/discharge cycling using a three-electrode cell with lithium counter and reference electrodes in 1 mol dm^{−3} LiClO₄ ethylene carbonate/diethyl carbonate (DEC) (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. The electrode was dried at 120 °C under vacuum overnight and pressed before electrochemical measurement. Prepared electrode consisted of 80 wt.% of petroleum coke sample and 20 wt.% PVdF. Potential scan rate was 1 mV s^{−1} for cyclic voltammetry and current densities were 60 and 150 mA g^{−1} for galvanostatic charge/discharge cycling. The electrochemical measurements were performed between 0 and 3 V versus Li/Li⁺ at 25 °C in a glove box filled by Ar.

3. Results and discussion

3.1. Composition and surface structure change of petroleum cokes by plasma-fluorination

The composition of petroleum cokes obtained by elemental analysis is given in Table 1. Original PC contained 2.9 at.% of hydrogen, which suggests that PC contains a small amount of oxygen as –COH and –CO(OH) [37]. The existence of sur-

Table 1
Composition of plasma-fluorinated petroleum cokes, obtained by elemental analysis

Fluorination time (min)	Sample	Composition (at.%)		
		C	F	O
0	PC	94.8	–	(2.3)
	PC1860	99.4	–	(0.6)
	PC2300	100.0	–	(0.0)
	PC2800	100.0	–	(0.0)
15	PC1860	100.0	0.0	(0.0)
	PC2300	100.0	0.0	(0.0)
	PC2800	100.0	0.0	(0.0)
30	PC1860	100.0	0.0	(0.0)
	PC2300	100.0	0.0	(0.0)
	PC2800	100.0	0.0	(0.0)
60	PC	96.5	0.7	(2.8)
	PC1860	100.0	0.0	(0.0)
	PC2300	100.0	0.0	(0.0)
	PC2800	100.0	0.0	(0.0)

Original PC contained 2.9 at.% of H. The parenthetical values are estimated value.

Table 2
Surface composition of plasma-fluorinated petroleum cokes, obtained by XPS

Fluorination time (min)	Sample	Surface composition (at.%)		
		C	F	O
0	PC	87.8	–	12.2
	PC1860	91.7	–	8.3
	PC2300	92.4	–	7.6
	PC2800	93.4	–	6.6
15	PC1860	86.9	1.5	11.6
	PC2300	85.5	4.1	10.4
	PC2800	81.3	8.1	10.6
30	PC1860	80.1	12.4	7.5
	PC2300	81.7	10.4	7.9
	PC2800	84.4	6.5	9.1
60	PC	54.2	35.7	10.1
	PC1860	74.3	15.8	9.9
	PC2300	77.2	12.0	10.8
	PC2800	83.2	7.4	9.4

face oxygen was shown by O1s XPS spectra as mentioned later. The fluorine contents were negligible except PC fluorinated for 60 min (0.7 at.%), being very different from those detected for the same petroleum cokes fluorinated by F₂ [37,38]. Table 2 shows the surface composition of petroleum coke samples, obtained by XPS. The fluorine concentration on the surface increased with increasing plasma-treatment time. At the beginning of plasma-fluorination (15 min-treatment), surface disordered parts were probably removed as fluorocarbon gases because the surface fluorine concentration became lower in the order of PC2800, PC2300 and PC1860. When plasma-treatment time was extended to 30 and 60 min, the surface fluorine concentration decreased with increasing heat-treatment temperature of petroleum coke from PC1860 or PC to PC2800. Petroleum cokes graphitized at the higher temperatures are more stable against fluorination. As already shown in a previous paper [39], the edge of oxygen containing petroleum coke is closed by carbon–carbon bond formation during the graphitization process at high temperatures of 2300–2800 °C. The closure of edge plane would occur by the elimination of surface oxygen as CO and recombination of bare carbon atoms. For this reason, the closed edge plane may be more stable also against plasma-treatment. This would be the reason why the surface fluorine concentration decreased with increasing graphitization temperature of petroleum coke, i.e. from PC1860 or PC to PC2800. The fluorine contents in Table 1 were lower than the values of 0.3–1.7 at.% obtained when the same petroleum cokes were fluorinated by F₂ [37,38]. The surface fluorine concentrations obtained for 60 min-treated samples in Table 2 were, however, close to those for the petroleum cokes fluorinated by F₂ at 300 °C [37,38]. It means that only surface layers of petroleum cokes were fluorinated by plasma-fluorination. On the other hand, no surface fluorine was found except one sample when the petroleum cokes were fluorinated by ClF₃ and NF₃ at 200–500 °C [40]. It is known that fluorination of organic compounds and carbon materials by F₂ is an electrophilic reaction, that is, F^{δ+} preferentially attacks C^{δ-} having a high electron density and F^{δ-} is bonded to another ele-

ment with a low electron density, yielding fluorinated graphene layers [49–51]. However, radical species such as CF₃ attack carbon atoms in plasma-fluorination using CF₄. Atoms and radicals such as F, Cl, ClF₂ and NF₂ generated by thermal decomposition of ClF₃ and NF₃ react with carbons in the fluorination using ClF₃ and NF₃ [40]. In such radical reactions, surface etching of carbon materials occurs, yielding fluorocarbon gases. Plasma-fluorination has the similar surface etching effect to that observed for the fluorination by ClF₃ and NF₃ at high temperatures. However, surface fluorine concentrations were much higher in the plasma-fluorination than in the fluorination by ClF₃ and NF₃. This may be ascribed to the low temperature of plasma-fluorination. The sample temperature was 90 °C in the case of plasma-fluorination while the fluorination with ClF₃ and NF₃ was done between 200 and 500 °C. The difference in the fluorine contents and surface fluorine concentrations due to the fluorination methods are thus attributed to the difference in the reaction mechanisms and temperatures. Surface oxygen was detected in all samples as given in Table 2. The surface oxygen concentrations were not largely changed before and after plasma-fluorination.

TEM observation was performed to confirm the surface structure change of graphitized petroleum cokes by plasma-fluorination. Fig. 1 shows TEM images obtained for PC2800 and those plasma-fluorinated for 15 and 60 min. The closed edges of non-fluorinated PC2800 are seen in Fig. 1(a), being formed by carbon–carbon bond formation with elimination of surface oxygen as CO during heat-treatment. The closed edges were observed in every part of the edge plane of PC2800. The same closed edges were also found in PC2300. It is seen in Fig. 1(b) that the closed edges were removed by surface etching. In PC2800 plasma-fluorinated for 60 min (Fig. 1(c)), the top of closed edges were destroyed and opened though closed edges were still observed. When plasma-fluorination of petroleum coke was made, a powder petroleum coke sample was placed in the center of the chamber. Therefore, plasma-treatment was not uniformly done to the surface of petroleum coke sample. In addition, TEM observation gives pictures of only local parts of the sample. This may be the reason why closed edges were observed in PC2800 plasma-fluorinated for 60 min as shown in Fig. 1(c). The increase in the surface disorder due to plasma-fluorination was found by Raman spectroscopy as shown in Table 3 as *R* values (=peak intensity ratios of D-band to G-band in Raman spectra). *R* value is a measure indicating the degree of surface disorder of carbon materials [52,53]. The increase in *R* values was larger in PC2300 and PC2800 than in PC1860. Plasma-

Table 3
R values (=I_D/I_G) calculated from Raman shifts of petroleum cokes and plasma-fluorinated samples

Plasma-fluorination time (min)	<i>R</i> (=I _D /I _G)			
	PC	PC1860	PC2300	PC2800
0	1.30	0.45	0.15	0.11
15	–	0.46	0.27	0.49
30	–	0.59	0.43	0.36
60	1.22	0.63	0.52	0.38

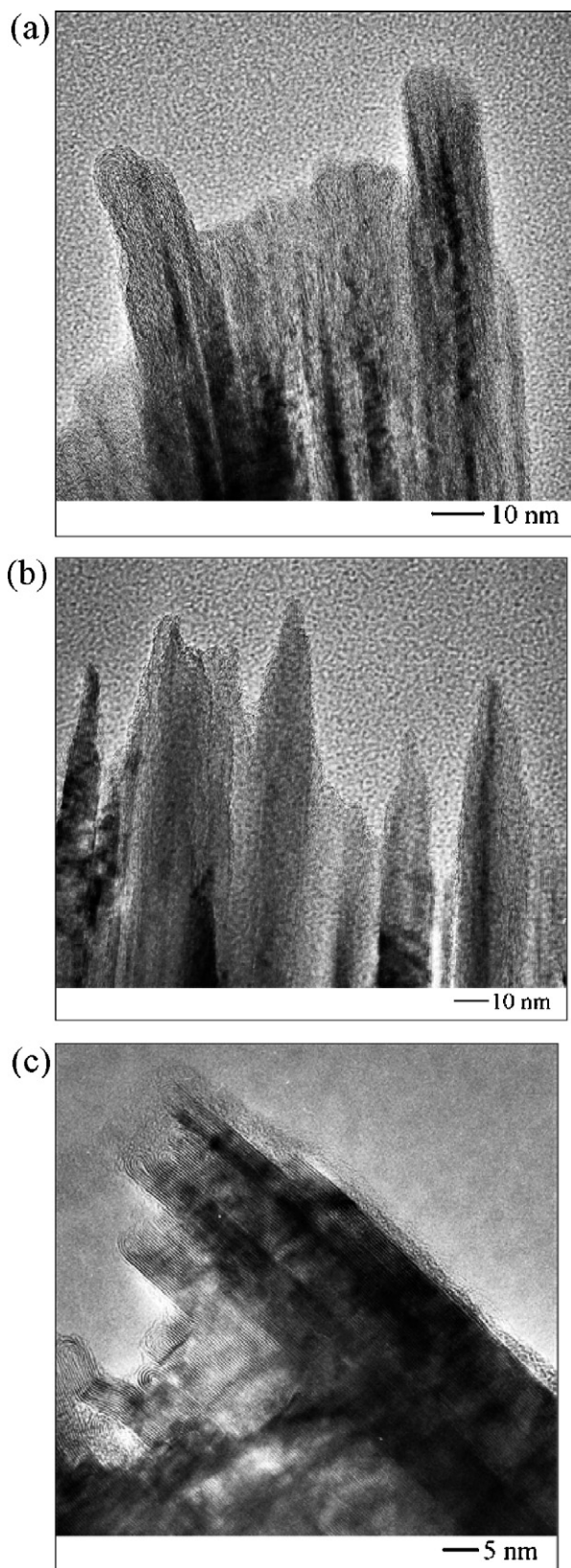


Fig. 1. Transmission electron microscopic images (TEM images) of PC2800 and those plasma-fluorinated for 15 and 60 min. (a) PC2800, (b) 15 min-fluorinated PC2800, (c) 60 min-fluorinated PC2800.

Table 4

Specific surface areas of petroleum cokes and plasma-fluorinated samples

Fluorination time (min)	Surface area ($\text{m}^2 \text{g}^{-1}$)			
	PC	PC1860	PC2300	PC2800
0	6.35	3.31	2.33	2.43
15	–	2.77	2.21	2.15
30	–	3.07	2.41	2.20
60	4.40	2.66	2.05	1.77

fluorination thus increases the surface disorder by destroying and opening the closed edge planes of graphitized petroleum cokes. BET surface area measurement indicated that the surface areas were somewhat decreased in most of the plasma-fluorinated samples due to surface etching effect by radical species produced in plasma as given in Table 4. Pore size distribution was also changed by plasma-treatment. Main change was the increase in surface meso-pores with diameter of 1.5–2 nm and decrease in those with diameter of 2–3 nm.

3.2. Electrochemical behavior of plasma-fluorinated petroleum cokes

First coulombic efficiencies of PC1860 heat-treated at a medium temperature of 1860 °C were high values of 90.2 and 88.2% at 60 and 150 mA g^{-1} , respectively. But those of PC2300 and PC2800 decreased to 71.9–70.0 and 65.4–63.6% with increasing heat-treatment temperature, respectively [37,38]. The decrease in the first coulombic efficiencies for non-fluorinated PC2300 and PC2800 is attributed to the closure of edge plane caused during graphitization process [39]. The closed edge plane hinders the smooth formation of SEI by electrochemical decomposition of a small amount of EC.

Plasma-fluorination gave a good effect to the electrode performance of graphitized petroleum cokes, i.e. PC2300 and PC2800 as shown in Figs. 2–4. No positive effect was found for low crystalline PC and PC1860. Fig. 2 shows the cyclic voltammograms obtained for PC2800 and plasma-fluorinated samples. Similar cyclic voltammograms were obtained for PC2300 and plasma-fluorinated samples. A large cathodic current peak was found at ca. 0.6 V versus Li/Li^+ at first cycle for non-fluorinated PC2800, indicating the electrochemical reduction of EC and subsequent formation of SEI. This cathodic peak was reduced with increasing plasma-treatment time as shown in Fig. 2. It means that SEI is formed by the decomposition of less amounts of EC. Fig. 3 shows charge/discharge potential curves obtained for PC2800 and those plasma-fluorinated for 15, 30 and 60 min. In consistency with the cyclic voltammograms, a potential plateau corresponding to the decomposition of EC was observed between 0 and 1 V at first cycle for non-fluorinated PC2800. The potential plateau between 0 and 1 V was clearly decreased by plasma-fluorination, which coincides well with the results obtained by cyclic voltammetry. Fig. 4 shows coulombic efficiencies for PC2300 and PC2800 as a function of cycle number. In the case of PC and PC1860, first coulombic efficiencies were not changed by 15 min plasma-treatment, slightly decreasing by 30 and 60 min treatments. As shown in Figs. 2–4, increase

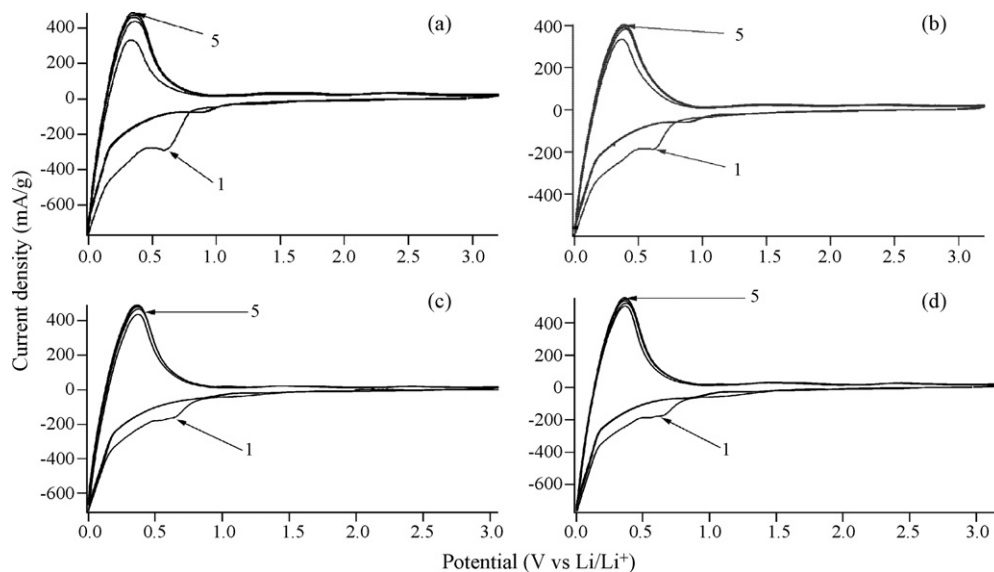


Fig. 2. Cyclic voltammograms for PC2800 and those plasma-fluorinated for 15, 30 and 60 min. (a) PC2800, (b) 15 min-fluorinated PC2800, (c) 30 min-fluorinated PC2800, (d) 60 min-fluorinated PC2800. 1: first cycle, 5: fifth cycle.

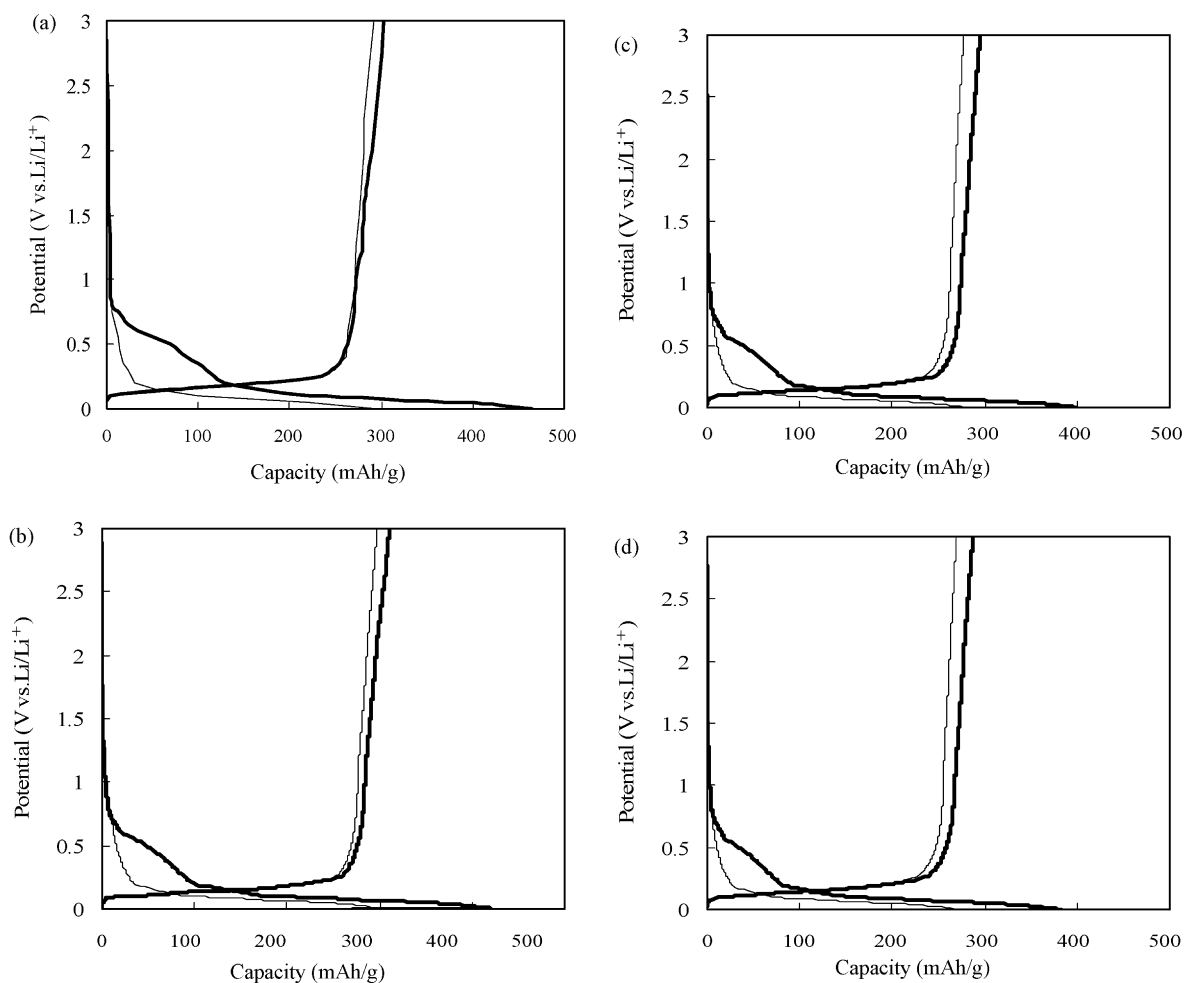


Fig. 3. Charge/discharge potential curves for PC2800 and those plasma-fluorinated for 15, 30 and 60 min, obtained at 60 mA g^{-1} . (a) PC2800, (b) 15 min-fluorinated PC2800, (c) 30 min-fluorinated PC2800, (d) 60 min-fluorinated PC2800. (—) first cycle, (---) 10th cycle.

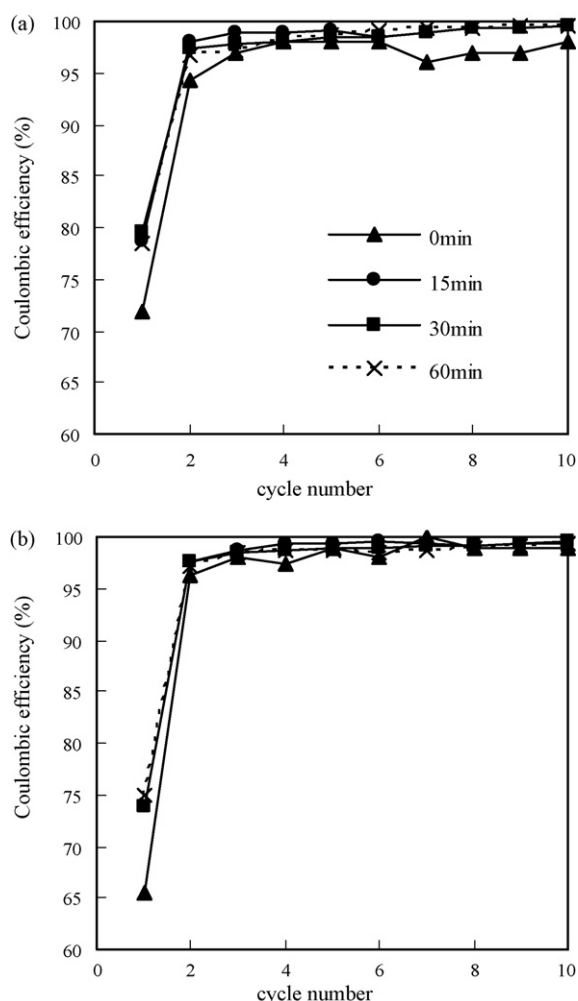


Fig. 4. Coulombic efficiencies for PC2300, PC2800 and those plasma-fluorinated for 15, 30 and 60 min, obtained at 60 mA g^{-1} as a function of cycle number. (a) PC2300 and plasma-fluorinated samples, (b) PC2800 and plasma-fluorinated samples. (▲) Non-fluorinated, (●) 15 min-fluorinated, (■) 30 min-fluorinated, (×) 60 min-fluorinated.

in the first coulombic efficiencies was found for graphitized PC2300 and PC2800. The increments of their first coulombic efficiencies were in the range of 6–8 and 8–10% for PC2300 and PC2800 at 60 mA g^{-1} , respectively. However, the charge capacities were not changed at 60 mA g^{-1} by the plasma-fluorination. Table 5 summarizes the results obtained for PC1860, PC2300 and PC2800 plasma-fluorinated for 30 min at 150 mA g^{-1} . The increments in first coulombic efficiencies of PC2300 and

Table 5
First charge capacities and first coulombic efficiencies of petroleum cokes plasma-fluorinated for 30 min at 150 mA g^{-1}

Sample	PC1860	PC2300	PC2800
First charge capacity (mAh g^{-1})			
Original	184	210	210
Plasma-fluorinated	239	220	203
First coulombic efficiency (%)			
Original	89.1	70.0	63.6
Plasma-fluorinated	85.4	78.0	72.5

PC2800 were 8.0 and 8.9%, respectively. In addition, first charge capacity of PC1860 was also increased by plasma-fluorination. As shown in Fig. 1, plasma-fluorination destroyed and removed the closed edge planes of graphitized petroleum cokes by radical reaction, increasing the surface disorder as given in Table 3. The increase in the surface disorder would enable the easy formation of SEI by the decomposition of less amounts of EC as shown in Figs. 2 and 3, which leads to the increase in first coulombic efficiencies, i.e. decrease in irreversible capacities. Impedance measurement made on petroleum cokes heat-treated at 2100 and 2600 °C showed that charge transfer resistance was reduced by surface fluorination while resistance of SEI was increased [39]. The increase in the resistance of SEI may be due to formation of a fluoride such as LiF. Influence of surface fluorination on SEI formation is probably similar to the previous case in which petroleum cokes were fluorinated by F_2 [39].

4. Conclusions

Effect of plasma-fluorination on the surface structure change and electrode performance of petroleum cokes has been investigated. Surface edge plane of oxygen containing petroleum coke is closed by carbon–carbon bond formation during the graphitization process. Closed edge planes of graphitized petroleum cokes gave a difficulty to smooth formation of SEI by the electrochemical decomposition of a small amount of EC, decreasing first coulombic efficiencies of PC2300 and PC2800 to 71.9–70.0 and 65.4–63.6%, respectively [37,38]. To change the surface structure of petroleum cokes, plasma-fluorination was performed for 15, 30 and 60 min using CF_4 gas. Fluorine contents obtained by elemental analysis were negligible except PC fluorinated for 60 min. However, surface fluorine concentrations obtained by XPS were similar to those observed in the fluorination by F_2 . It shows that only surface was fluorinated by plasma-fluorination. TEM observation of plasma-fluorinated PC2800 revealed that the closed edge plane was removed and opened by plasma-fluorination. BET surface areas were slightly decreased by surface etching effect. R values calculated from two Raman shifts indicated that the surface disorder of heat-treated petroleum cokes was increased by plasma-treatment. Cyclic voltammograms obtained for PC2300 and PC2800 demonstrated that cathodic current peaks indicating the reduction of EC were significantly reduced by plasma-fluorination. The results of galvanostatic charge/discharge experiments coincided well with those obtained by cyclic voltammetry, showing that first coulombic efficiencies of PC2300 and PC2800 increased by 6–8 and 8–10% at both 60 and 150 mA g^{-1} , respectively.

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