Surface structure and electrochemical properties of surface-fluorinated petroleum cokes for lithium ion battery

Tsuyoshi Nakajima[*], Jianling Li, Kazuhisa Naga, Kiyomi Yoneshima,
Takatomo Nakai, Yoshimi Ohzawa

Department of Applied Chemistry, Aichi Institute of Technology, Yakusa-cho, Toyota-shi 470-0392, Japan

Abstract

Surface structure and electrochemical behavior of surface-fluorinated petroleum coke samples (original petroleum coke and those heat-treated at 1860, 2300 and 2800 °C, abbreviated to original PC, PC1860, PC2300 and PC2800, respectively) have been investigated. Surface fluorination of petroleum cokes by elemental fluorine reduced surface oxygen. Surface areas of fluorinated petroleum cokes were nearly the same as those of non-fluorinated ones or only slightly increased by fluorination except original PC fluorinated at 300 °C. Total meso-pore volumes of fluorinated samples showed the same trend. The charge capacity of non-fluorinated petroleum coke was increased by heat-treatment at 2300 and 2800 °C. However, the first coulombic efficiency was the highest, 90–89% in PC1860, decreasing to 72–70 and 65–64% for PC2300 and PC2800, respectively. It is noted that first coulombic efficiencies were increased by 12–18% for PC2300 and PC2800 fluorinated at 300 °C.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

Surface modification is one of the effective methods for improving the electrochemical characteristics of carbonaceous electrodes for lithium ion battery. Electrode characteristics are governed by crystallinity, surface area, surface pore volume distribution, surface chemical species such as oxygen and so on. Several methods of surface modification were applied to improve electrochemical behavior of carbon materials. They are surface oxidation [1–3], surface fluorination [4–8], thin metal coating [9] and carbon coating [10–14]. Light oxidation of carbon materials caused increase in their capacities by forming nanochannels at the surface while strong oxidation degraded surface structure, leading to increase in the irreversible capacity [1–3]. Carbon coating is an effective method for increasing the capacity and first coulombic efficiency [10–14]. Rotation of a reactor was recently attempted to obtain a uniformly coated carbon layer [13]. Chemical vapor infiltration (CVI) of pyrolytic carbon into a porous carbon material is effective to increase first coulombic efficiency [14]. It has been shown

that surface fluorination increases the capacities of natural graphite samples with different particle sizes [4–8]. 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 capacities without decrease in first coulombic efficiencies [4–6,8]. Plasma fluorination using CF_4 also gave the same results for natural graphite powder [7]. The larger capacities than the theoretical value of graphite, 372 mAh g^{-1} were obtained for surface-fluorinated graphite samples [4–8]. In the present study, surface structure change of petroleum cokes by fluorination was investigated and electrochemical characteristics of surface-fluorinated samples were evaluated by cyclic voltammetry and galvanostatic charge/discharge cycling.

2. Experimental

2.1. Composition and surface structure analysis of fluorinated petroleum cokes

The starting materials were petroleum coke and those heat-treated at 1860, 2300 and 2800 °C (abbreviated to original PC, PC1860, PC2300 and PC2800, respectively). The *d*-spacing of (0 0 2) diffraction lines were 0.3450, 0.3385,

* Corresponding author. Tel.: +81-565-48-8121ex2201;
fax: +81-565-48-0076.
E-mail address: nakajima-san@aitech.ac.jp (T. Nakajima).

0.3366 and 0.3361 nm for original PC, PC1860, PC2300 and PC2800, respectively (Shimadzu XD-610, Cu Kα). The d-values were decreased with increasing heat-treatment temperature, indicating the increase in the crystallinity. However, all these values were larger than that of natural graphite, 0.3354 nm.

The surface fluorination of petroleum coke (150 mg) was made at 150, 200 and 300 °C by 3×10^4 Pa elemental fluorine (purity: 99.4–99.7%) for 2 min, using a nickel reactor. The composition of surface-fluorinated samples was determined by elemental analyses of C, H and F, which were performed at Elemental Analysis Center of Faculty of Pharmaceutical Sciences of Kyoto University. The surface composition was also obtained by X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA 1000). The surface areas and surface pore volume distribution were measured by BET method using nitrogen adsorption (Micromeritics, Gemini 2375).

2.2. Electrochemical measurements

Three electrodes cell with petroleum coke as a working electrode and metallic lithium as counter and reference electrodes were used for cyclic voltammetry and galvanostatic charge/discharge cycling. The preparation of a working electrode was described elsewhere [4]. The electrolyte solution was 1 mol dm^{-3} LiClO$_4$–ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v). Cyclic voltammetry was done at a scan rate of 1 mV s^{-1} between 0 and 4 V relative to Li/Li$^+$. Galvanostatic charge/discharge was performed at current densities of 60 and 150 mA g^{-1}. These electrochem-

ical measurements were carried out at 25 °C in a glove box filled with argon.

3. Results and discussion

3.1. Composition of surface-fluorinated petroleum cokes

The results of elemental analysis of surface-fluorinated petroleum coke samples are given in Table 1. Fluorine contents were relatively higher in original 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 PC1860, PC2300 and PC2800 fluorinated at 150 and 200 °C were in the detection limit (<0.2 at.%). This suggests a large difference in crystallinity between original and heat-treated petroleum cokes. The fluorine contents were in the range of 0.3–0.6 at.% for PC1860, PC2300 and PC2800 fluorinated at 300 °C.

Table 2 shows binding energies of C 1s, O 1s and F 1s electrons and surface composition of petroleum coke samples and those fluorinated at 300 °C. The binding energies for F 1s electron are close to that for C–F covalent bond (binding energy of F1s electron: 689–690 eV) though they decreased from 688.8 to 687.3 eV with increasing crystallinity of petroleum coke [15,16]. Corresponding to the F 1s peaks, weak shifted peaks of C 1s electron were observed at 290.1 and 288.6 eV for fluorinated samples of original PC and PC1860, respectively. This is because fluorination reaction well proceeds for a carbon material with a low crsytallinity.

Table 1
Composition (at.%) of surface-fluorinated petroleum cokes

Fluorination temperature	Heat-treatment temperature of petroleum coke											
	Original			1860 °C			2300 °C			2800 °C		
	C	F	O	C	F	O	C	F	O	C	F	O
Original	94.8	2.9[a]	(2.3)	99.4	–	(0.6)	100.0	–	(0.0)	100.0	–	(0.0)
150 °C	96.7	0.9	(2.4)	99.8	0.0	(0.2)	100.0	0.0	(0.0)	99.8	0.0	(0.2)
200 °C	96.5	1.2	(2.3)	99.8	0.0	(0.2)	100.0	0.0	(0.0)	99.8	0.0	(0.2)
300 °C	90.4	7.3	(2.3)	99.2	0.6	(0.2)	99.6	0.3	(0.1)	99.5	0.4	(0.1)

0: within detection limit (<0.2 at.%).
[a] Hydrogen contained in original petroleum coke. No hydrogen was detected in heat-treated petroleum cokes.

Table 2
Binding energies of C 1s, O 1s and F 1s electrons (eV) and surface composition (at.%) of fluorinated petroleum cokes

Fluorination temperature	Heat-treatment temperature of petroleum coke											
	Original			1860 °C			2300 °C			2800 °C		
	C	O	F	C	O	F	C	O	F	C	O	F
Original	284.3	531.7	–	284.3	531.7	–	284.3	531.7	–	284.3	531.9	–
300 °C	285.3, 290.1	531.9	688.8	284.1, 288.6	531.9	687.6	284.1	531.8	687.6	284.1	531.8	687.3
Original	87.8	12.2	–	91.7	8.3	–	92.4	7.6	–	93.4	6.6	–
300 °C	44.8	5.0	50.2	72.7	4.9	22.4	81.8	6.5	11.7	89.2	5.6	5.2

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

Fluorination temperature	Heat-treatment temperature of petroleum coke			
	Original	1860 °C	2300 °C	2800 °C
Original	6.35	3.31	2.33	2.43
150 °C	7.35	3.03	2.21	2.85
200 °C	8.06	3.31	2.27	2.73
300 °C	25.2	3.20	2.25	2.81

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 2. The surface oxygen of natural graphite powder ($\approx 7 \mu m$) was 6 at.% when Shimazu ESCA 1000 spectrometer was used in the present study. However, it was 1.5–2.0 at.% when Ulvac Phi Model 5500 spectrometer was used before [4]. 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 2, that is, those of non-fluorinated and fluorinated samples are estimated to be approximately in the range of 2.6–8.2 and 0.9–2.5 at.%, respectively. The amounts of surface fluorine significantly decreased from 50.2 to 5.2 at.% with increasing crystallinity of petroleum coke, which reflects the reactivity of elemental fluorine with petroleum coke samples.

3.2. Surface structure change of petroleum cokes by fluorination

The BET surface areas and total meso-pore volumes of petroleum cokes and surface-fluorinated samples are summarized in Tables 3 and 4. The surface area of original PC is large, however, decreasing to half or less than half by heat-treatment. The meso-pore volumes were also reduced by heat-treatment in the same manner. The surface areas and meso-pore volumes were changed by surface fluorination. However, the result was somewhat different depending on the crystallinity of petroleum cokes. Surface area of original PC was slightly increased by the fluorination at 150 and 200 °C, and large increase was observed for the sample fluorinated at 300 °C. The increase in the surface area seems to be proportional to the fluorine content in the sample. A low crystalline carbon with a large surface area is easily fluori-

Table 4
Total meso-pore volumes ($10^{-4} cm^3 g^{-1}$) of surface-fluorinated petroleum cokes

Fluorination temperature	Heat-treatment temperature of petroleum coke			
	Original	1860 °C	2300 °C	2800 °C
Original	167	79.5	59.3	59.9
150 °C	128	78.5	64.3	68.8
200 °C	140	76.4	56.6	64.5
300 °C	204	111	53.5	74.2

nated, forming a covalently bonded C–F layers, though the highly disordered parts may be lost by the fluorination as CF_4 gas. The formation of graphite fluoride layers enlarges the surface area [17].

Surface fluorination of PC1860 and PC2300 gave slightly different results. Surface areas of the fluorinated petroleum cokes were almost the same as or slightly smaller than those before fluorination. The meso-pore volumes had the similar trend. Heat-treatment of carbon materials reduces their structural disorder and simultaneously surface areas. Fluorination rate of heat-treated petroleum cokes slowed down under the same fluorination condition. Disordered parts were mainly eliminated in the samples fluorinated at 150 and 200 °C, and the fluorination level was slightly higher at 300 °C. 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% [5–8]. 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.

Fig. 1 shows change in the pore volume distribution by surface fluorination. The pore volumes were significantly decreased by heat-treatment as also shown in Table 3. Fluorination eliminates disordered parts at the surface as CF_4 gas and causes carbon–carbon bond rupture leading to the formation of CF_2/CF_3 groups. In case of original PC, meso-pores with diameters of 7–8 and 8–9 nm were increased by fluorination, in particular those with diameter of 2–3 nm were highly increased for the sample fluorinated at 300 °C, while the meso-pores with diameter of 2–3 nm were decreased by fluorination for PC1860 and PC2300, and nearly the same for PC2800. However, the meso-pores with diameters between 5 and 15 nm were irregularly increased in case of heat-treated petroleum cokes. Among the observed meso-pores, relatively small ones with diameters of 5–10 nm were formed at different fluorination temperatures depending on the heat-treatment temperatures of petroleum cokes. The optimum fluorination temperature to yield meso-pores with diameters of 5–10 nm was elevated from 150 to 300 °C with increasing heat-treatment temperature of petroleum coke from 1860 to 2800 °C. To create small meso-pores, the higher temperature is needed for petroleum coke with the higher crystallinity.

3.3. Cyclic voltammetry study on the surface-fluorinated petroleum cokes

The cyclic voltammograms for four kinds of petroleum cokes and surface-fluorinated samples are shown in Fig. 2. A large irreversibility was observed in the reduction and oxidation currents for original PC. The reduction current started to flow at 1.2 V and oxidation current was observed until about 1.5 V relative to Li/Li$^+$. The peak currents were 500 mA g^{-1} at peak potentials, 0.46–0.53 V in oxidation process. The peak potential shifted from 0.53 to 0.46 V with increasing cycling. On the other hand, heat-treated petroleum cokes
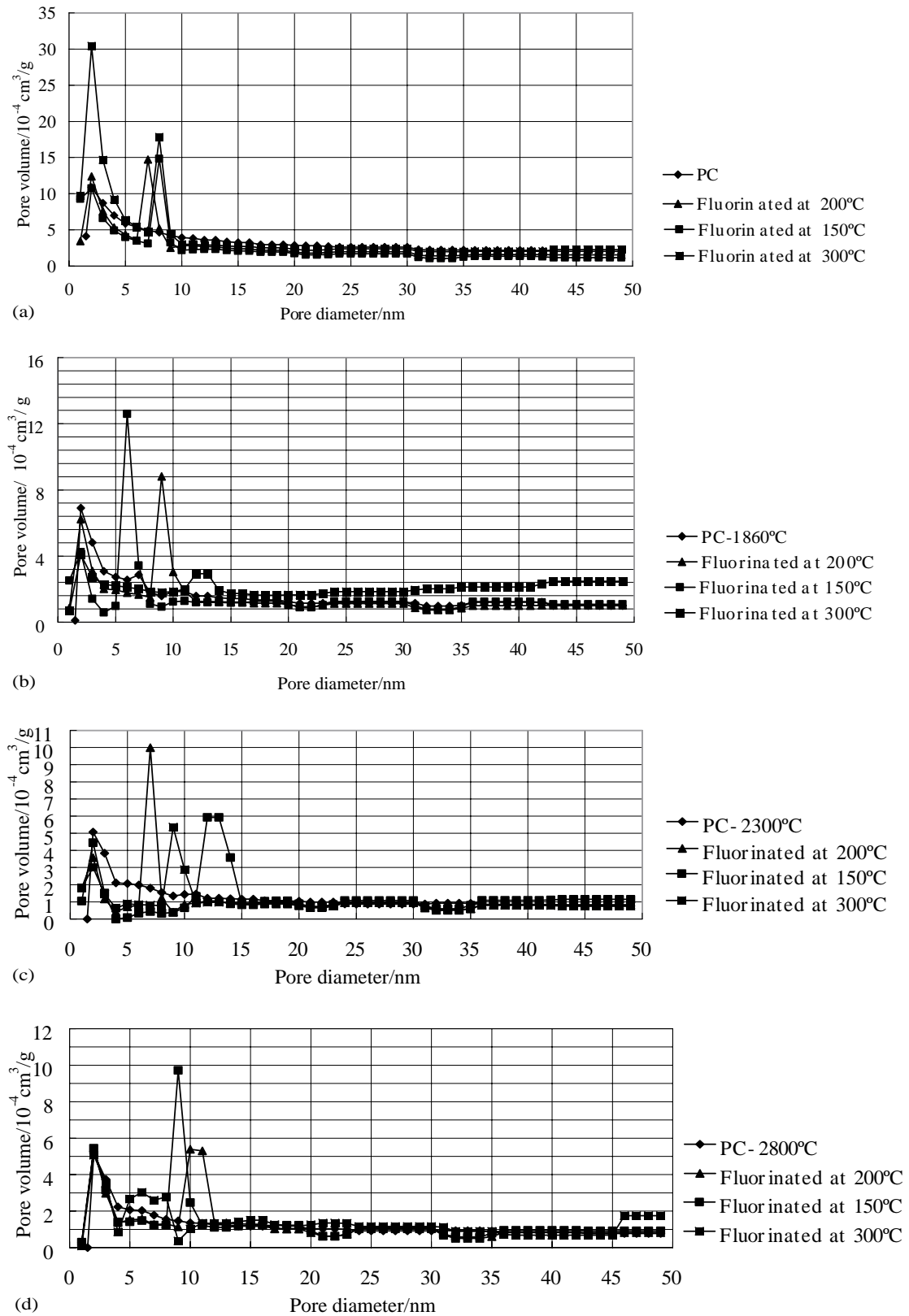
Fig. 1. Pore volume distribution of original and heat-treated petroleum coke (PC) samples and those fluorinated at 150, 200 and 300 °C: (a) original petroleum coke and fluorinated samples, (b) petroleum coke heat-treated at 1860 °C and fluorinated samples, (c) petroleum coke heat-treated at 2300 °C and fluorinated samples, (d) petroleum coke heat-treated at 2800 °C and fluorinated samples.
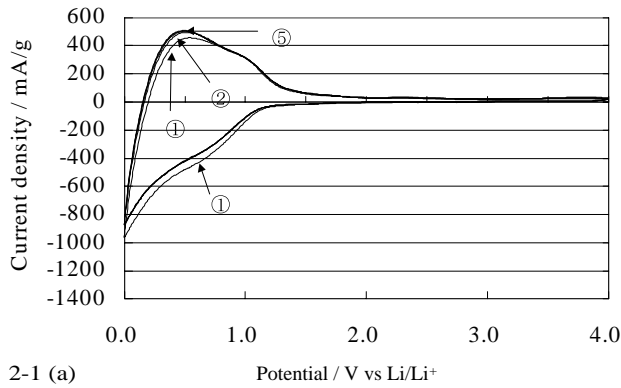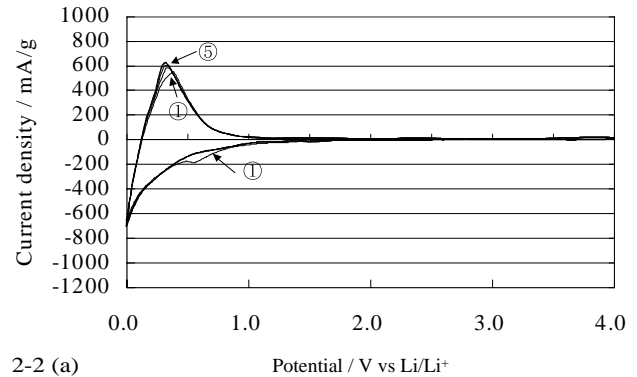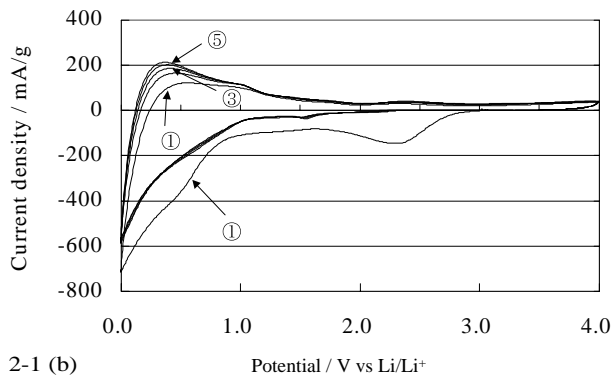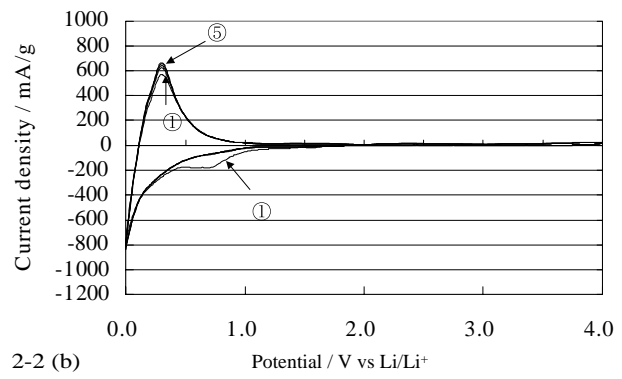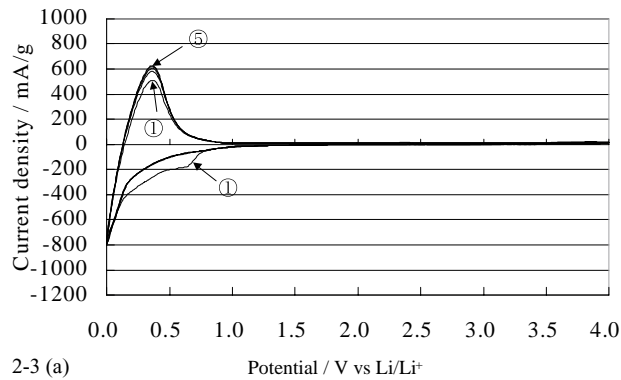
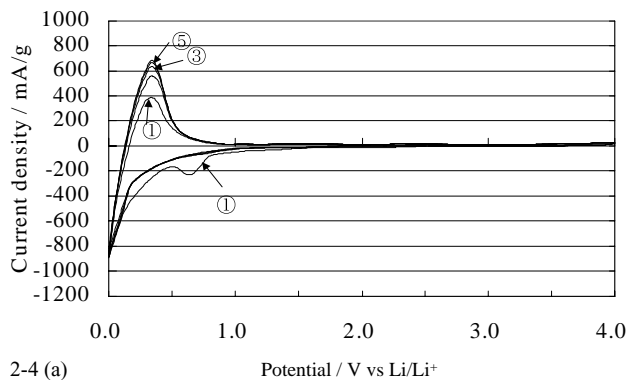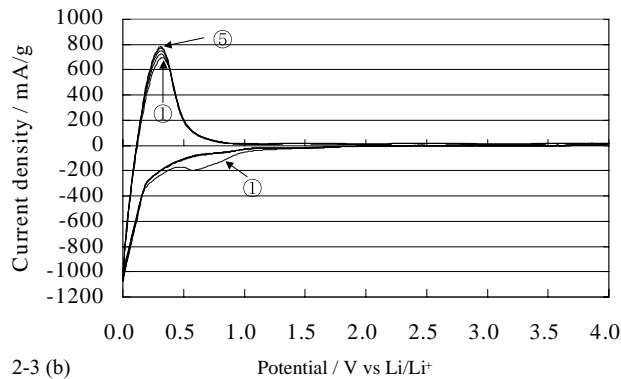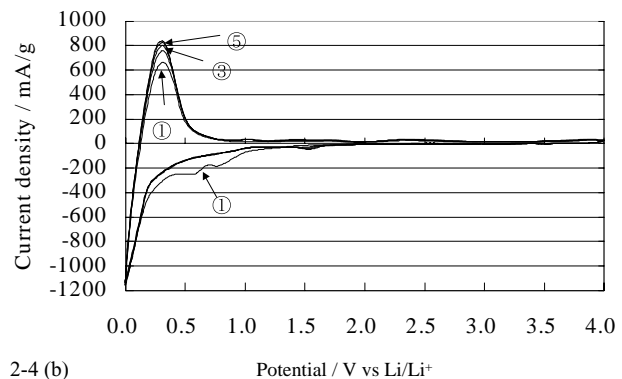Fig. 2. Cyclic voltammograms for original and heat-treated petroleum cokes and those fluorinated at 300 °C: (2-1) original petroleum coke (a) and that fluorinated at 300 °C (b); (2-2) petroleum coke heat-treated at 1860 °C (a) and that fluorinated at 300 °C (b); (2-3) petroleum coke heat-treated at 2300 °C (a) and that fluorinated at 300 °C (b); (2-4) petroleum coke heat-treated at 2800 °C (a) and that fluorinated at 300 °C (b). (1) First cycle, (2) second cycle, (3) third cycle, (5) fifth cycle.

exhibited the higher reversibility in reduction and oxidation currents (Fig. 2-1(a), 2-2(a), 2-3(a) and 2-4(a)). The potentials at which reduction currents started to increase and oxidation currents almost disappeared were shifted to lower potentials. The oxidation peak currents increased to 600 mA g^{-1} or more, and peak potentials were located at 0.32–0.36, 0.36 and 0.35 V for PC1860, PC2300 and PC2800, respectively. In the first reduction process, a reduction peak indicating the formation of solid electrolyte interface (SEI) is observed at 0.60 V [18]. In the present study, reduction peaks appeared at 0.55–0.60 V for heat-treated petroleum cokes though it was not clearly observed for original PC. The reduction peak indicating SEI formation was the smallest for PC1860 and increased with increasing heat-treatment temperature from 1860 to 2800 °C (Fig. 2-2(a), 2-3(a) and 2-4(a)). The formation of SEI proceeds with intercalation of solvated lithium ion into surface region of a carbonaceous electrode and subsequent decomposition of the solvents [19,20]. The results suggest that the SEI formation is easier for a carbon with moderate graphitization degree.

The fluorination degree was higher for original PC than other heat-treated petroleum cokes as already mentioned. Cyclic voltammogram for original PC fluorinated at 300 °C shows a large reduction current at ca. 2.3 V in first reduction curve as shown in Fig. 2-1(b). The reduced fluorine atoms would be those bonded to basal plane of carbon because fluorinated carbon having a large amount of fluorine atoms at its edge plane has a small discharge capacity between 2 and 3 V versus Li/Li$^+$ as a cathode of primary lithium battery [21]. This suggests that fluorine atoms bonded to edge plane of a carbon material are more stable than those bonded to basal plane. The oxidation peaks were observed at 0.36–0.50 V lower than 0.46–0.53 V for original PC though the peak currents were low. Surface fluorination of heat-treated petroleum cokes gives several positive effects to their electrochemical behavior. Oxidation peaks were observed at 0.32 V for PC1860 and PC2300 and 0.31 V for PC2800. Thus, the peak potentials were slightly shifted to the lower values and the peak currents were increased by surface fluorination. This means that the reversibility of lithium ion intercalation and deintercalation into and from petroleum coke was improved by surface fluorination. No reduction currents were observed at around 2.5 V for any of heat-treated petroleum cokes.

In addition to the reduction peaks at 0.55–0.60 V indicating the decomposition of EC and subsequent formation of SEI, the other reduction peak was clearly observed at 0.76 V in the first reduction curve for fluorinated PC2800 (Fig. 2-4(b)). The same peak was also observed for surface-fluorinated carbon film [22]. In the present study, no reduction peak was observed at 0.8 V before fluorination and from second cycle for the surface-fluorinated sample (Fig. 2-4). Only a trace amount of fluorine (0.2 at.%) was detected by XPS analysis for surface-fluorinated graphite samples after they were subjected to charge/discharge cycling

between 0 and 3 V versus Li/Li$^+$ [4]. This means that surface fluorine is reduced as LiF by the reaction with lithium:

$$CF + Li^+ + e^- \rightarrow C + LiF \qquad (1)$$

Considering these results, one possible interpretation for the reduction peak observed at 0.76 V is that fluorine bonded to the surface of carbon is electrochemically reduced at ca. 0.8 V versus Li/Li$^+$.

Fluorination reaction replaced surface oxygen to fluorine by 7.2–1.0 at.% as given in Table 2. Reduction of fluorine would facilitate the formation of SEI with LiF, giving a new carbon surface with less amount of oxygen.

3.4. Charge/discharge characteristics of surface-fluorinated petroleum cokes

Potential curves for original PC gradually decreased and increased with intercalation and deintercalation of lithium ion, respectively (Fig. 3-1(a)). However, the profile of potential curves for heat-treated petroleum cokes was rather similar to that for natural graphite as shown in Fig. 3-2(a). The charge capacities of original PC and PC1860 were in the range of 246–258 mAh g^{-1} and those of PC2300 and PC2800 were in the range of 285–306 mAh g^{-1} at 60 mA g^{-1}. The capacities of heat-treated petroleum cokes were in the range of 180–218 mAh g^{-1} at 150 mA g^{-1}. These values are lower than ca. 360 mAh g^{-1} of natural graphite powder at a current density of 60 mA g^{-1} [4–8]. This may be because graphitized petroleum cokes have a lower crystallinity than natural graphite as shown by $d(0\,0\,2)$ values. When crystallinity of a carbon material is relatively low (original PC and PC1860 in the present study), amount of lithium ions accommodated between two graphene layers is relatively small because the carbon takes a turbostratic structure [23]. Heat-treatment at higher temperatures than 2000 °C improves the crystallinity of a carbon material and increases the capacity. For this reason, PC2300 and PC2800 possess the higher capacities than original PC and PC1860. Tables 1 and 2 indicate that original PC was highly fluorinated at 300 °C. The discharge of fluorine is observed between 2.7 and 1.0 V as shown in Fig. 3-1(b). However, the potential profile was unchanged by surface fluorination in case of PC2800 except the first discharge curves below 1 V (Fig. 3-2). PC2300 and PC2800 also represented similar potential curves at a current density of 150 mA g^{-1} as shown in Fig. 4. Tables 5 and 6 show the effect of surface fluorination on the charge capacities at 60 and 150 mA g^{-1}, respectively. It was found that surface fluorination did not give a positive effect to charge capacities of petroleum cokes except one sample (PC2800 fluorinated at 300 °C in Table 6), which gave 10.9–16.7% higher capacities than non-fluorinated one.

First coulombic efficiencies of non-fluorinated petroleum cokes varied depending on the heat-treatment temperatures, that is, the crystallinity of petroleum coke samples. PC1860 exhibited high first coulombic efficiencies, 90.2–89.1%.
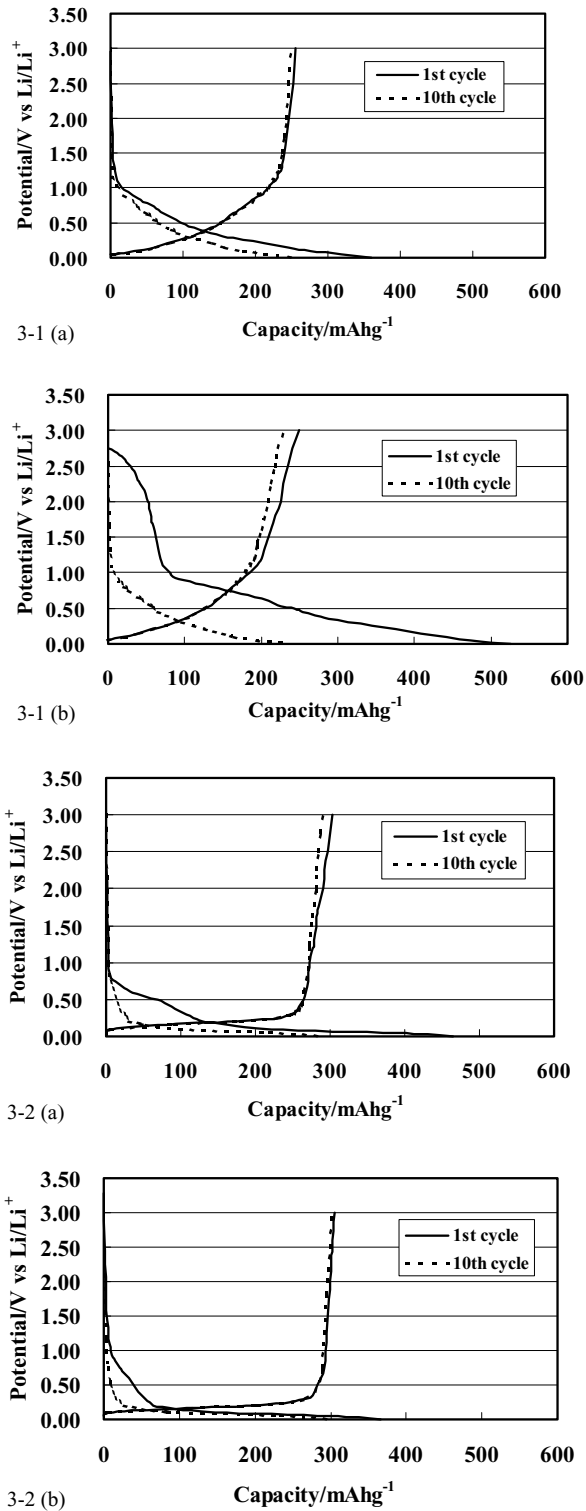
Fig. 3. Charge/discharge curves for petroleum coke samples and those fluorinated at 300 °C, obtained at a current density of 60 mA g^{-1}: (3-1) original petroleum coke (a) and that fluorinated at 300 °C (b); (3-2) petroleum coke heat-treated at 2800 °C (a) and that fluorinated at 300 °C (b).
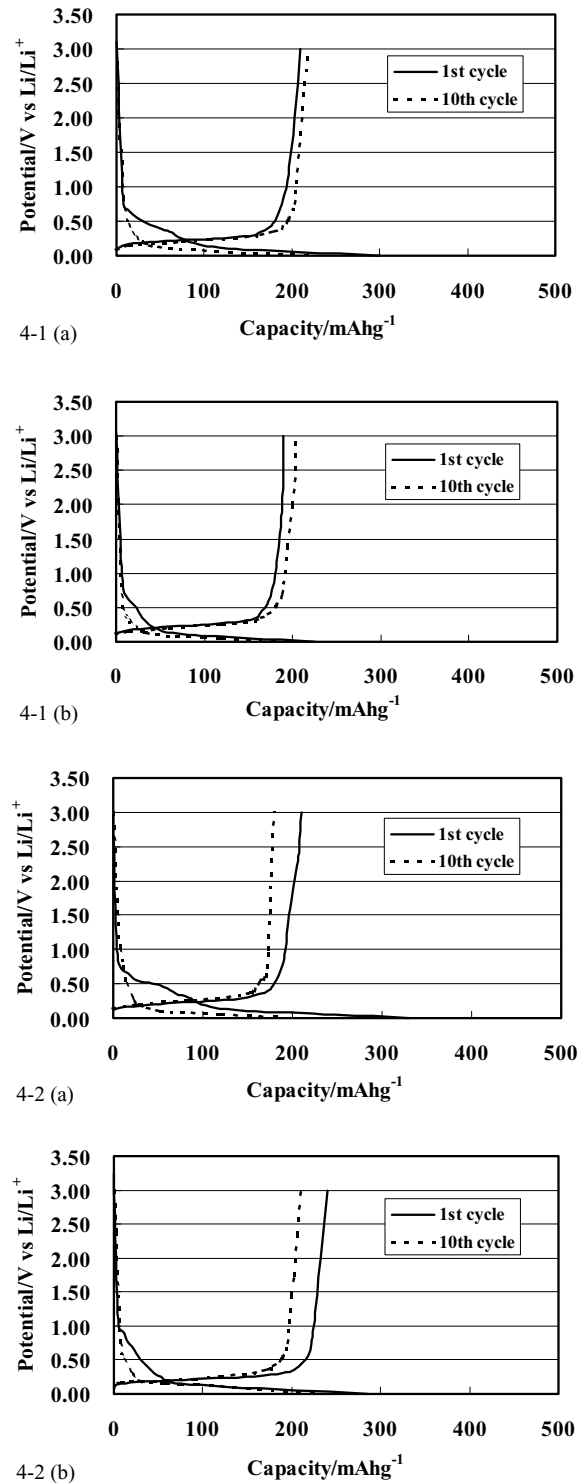
Fig. 4. Charge/discharge curves for petroleum cokes heat-treated at 2300 and 2800 °C and those fluorinated at 300 °C, obtained at a current density of 150 mA g^{-1}: (4-1) petroleum coke heat-treated at 2300 °C (a) and that fluorinated at 300 °C (b); (4-2) petroleum coke heat-treated at 2800 °C (a) and that fluorinated at 300 °C (b).

Table 5
Charge capacities (mAh g^{-1}) of petroleum coke samples at first and 10th cycles, obtained at a current density of 60 mA g^{-1}

Fluorination temperature	Heat-treatment temperature of petroleum coke			
	Original	1860 °C	2300 °C	2800 °C
Original	258–246	249–246	300–285	306–291
150 °C	249–243	240–237	297–285	312–291
200 °C	249–234	240–237	291–282	312–291
300 °C	249–231	240–240	285–285	306–300

Table 7
First coulombic efficiencies (%) for petroleum coke samples at a current density of 60 mA g^{-1}

Fluorination temperature	Heat-treatment temperature of petroleum coke			
	Original	1860 °C	2300 °C	2800 °C
Original	72.3	90.2	71.9	65.4
150 °C	68.6	87.9	72.8	61.5
200 °C	68.6	87.9	72.4	60.5
300 °C	47.4	83.3	84.1	83.6

However, first coulombic efficiencies were decreased with increasing heat-treatment temperature of petroleum coke, that is, 71.9–70.0 and 65.4–63.6% for PC2300 and PC2800, respectively, while natural graphite samples with high crystallinity exhibited high first coulombic efficiencies of 80–85% [4–8]. The first coulombic efficiencies obtained for petroleum cokes well coincide with those obtained by cyclic voltammetry. As already shown in Fig. 2, the reduction peak of EC at 0.6 V was the smallest for PC1860, and increased for PC2300 and PC2800. This means that somewhat disordered surface is preferable for accommodating solvated lithium ions in the surface region and subsequent decomposition of the solvents to form SEI. It was recently reported by high resolution transmission electron microscopic study that edge plane of heat-treated carbon is closed by carbon–carbon bond formation [24], which would give some difficulty to electrochemical insertion of solvated lithium ion into surface region of a carbon material. This may be the main reason why the first coulombic efficiencies of PC2300 and PC2800 were lower than that for PC1860. On the other hand, natural graphite powder is prepared by pulverization of flake sample. Therefore, its surface may be open though some oxygen atoms are bonded.

An interesting result obtained in the present study is that first coulombic efficiencies were significantly increased by surface fluorination for PC2300 and PC2800 as given in Tables 7 and 8. The first coulombic efficiencies were increased by 12.2–18.2% when they were fluorinated at 300 °C, and those of PC2300 fluorinated at 150 and 200 °C were increased by 0.5–6.5%. This is also shown in Figs. 3-2, 4-1 and 4-2, in which the potentials at first cycle quickly lowered below 1 V for surface-fluorinated samples.

Several factors should be considered for the increase in first coulombic efficiencies of PC2300 and PC2800 by

fluorination. They are surface structure and influence of surface chemical species such as fluorine and oxygen. In case of natural graphite powder with high crystallinity, first coulombic efficiencies were almost the same as those of non-fluorinated samples when fluorinated between 150 and 300 °C notwithstanding the surface areas were increased by 17–77% [4–8]. On the other hand, the surface areas were slightly decreased by fluorination for PC2300 and somewhat increased for PC2800. The increase in the surface areas was only ∼17% for PC2800 (Table 3) because surface disordered part is eliminated as CF_4 gas. Since enlargement of electrode area facilitates a reaction rate, it is expected that reduction of EC is more accelerated at the surface of fluorinated natural graphite powder than fluorinated petroleum coke samples. Increase in the surface area by fluorination will give a disadvantage to first coulombic efficiency. Nevertheless, the coulombic efficiencies were nearly the same after surface fluorination for natural graphite powder when it was fluorinated between 150 and 300 °C. Surface fluorination of natural graphite samples increased small meso-pores with diameters of 2–3 nm [5,6], which can make easier the accommodation of solvated lithium ion in the surface region of graphite and formation of SEI. On the other hand, the change in the surface areas was small before and after fluorination in case of PC2300 and PC2800. This is an advantage for heat-treated petroleum cokes because electrochemical decomposition of EC does not increase. Another advantage given by fluorination would be the increase in surface disorder of PC2300 and PC2800 by carbon–carbon bond breaking. Edge plane closed by carbon–carbon bond formation due to heat-treatment would be opened by fluorination reaction with formation of CF_2/CF_3 groups. The opening of edge plane can make easy the accommodation of solvated lithium ion at edge surface to facilitate the SEI formation.

Table 6
Charge capacities (mAh g^{-1}) of petroleum coke samples at first and 10th cycles, obtained at a current density of 150 mA g^{-1}

Fluorination temperature	Heat-treatment temperature of petroleum coke		
	1860 °C	2300 °C	2600 °C
Original	184–195	210–218	210–180
150 °C	165–173	180–150	218–188
200 °C	165–180	195–165	210–180
300 °C	169–180	188–203	233–210

Table 8
First coulombic efficiencies (%) for petroleum coke samples at a current density of 150 mA g^{-1}

Fluorination temperature	Heat-treatment temperature of petroleum coke		
	1860 °C	2300 °C	2800 °C
Original	89.1	70.0	63.6
150 °C	88.0	75.0	54.7
200 °C	88.0	76.5	59.6
300 °C	81.8	83.3	79.5

Adsorption of a polar solvent molecule such as EC may have a difficulty on surface-fluorinated petroleum cokes due to the hydrophobic nature of CF_2 and CF_3 groups with covalent bonds. Fluorine atoms bonded to graphite surface is finally removed as LiF by the electrochemical reduction because the amount of fluorine detected by XPS analysis was only 0.2 at.% after charge/discharge cycling [4]. LiF thus formed on petroleum coke would facilitate the SEI formation as one of the constituents of SEI.

The other effect of surface fluorination would be the decrease in the amounts of surface oxygen. Some of surface oxygen atoms are replaced by fluorine as shown in Table 2. The decrease in the surface oxygen by fluorination was 1.1–1.0 at.% for PC2300 and PC2800. Since surface oxygen interacting with lithium ion is one of the factors to increase the irreversible capacity, replacement of surface oxygen to fluorine is found to give a positive effect to first coulombic efficiency.

4. Conclusion

Effect of surface fluorination on the surface structure and electrochemical characteristics changes depending on the crystallinity and surface structure of petroleum cokes. Surface areas of petroleum coke samples were nearly the same as those of non-fluorinated ones or slightly increased by surface fluorination because the crystallinity is not as high as that of natural graphite even in PC2800. Surface fluorination by elemental fluorine also reduced surface oxygen interacting with lithium ion. In addition, surface fluorination increases surface disorder of graphitized carbon materials [4–7], that is, would open the edge plane by carbon–carbon bond breaking to yield CF_2/CF_3 groups, which makes easier the accommodation of lithium ions in the surface region of carbon. These factors would reduce the electrochemical decomposition of EC and facilitate the SEI formation, leading to the high coulombic efficiencies of PC2300 and PC2800 fluorinated at 300 °C.

Acknowledgements

References

[1] J.S. Xue, J.R. Dahn, J. Electrochem. Soc. 142 (1995) 3668.
[2] E. Peled, C. Menachem, D. Bar-Tow, A. Melman, J. Electrochem. Soc. 143 (1996) L4.
[3] M. Hara, A. Satoh, N. Tamaki, T. Ohsaki, Tanso 165 (1994) 261.
[4] T. Nakajima, M. Koh, R.N. Singh, M. Shimada, Electrochim. Acta 44 (1999) 2879.
[5] V. Gupta, T. Nakajima, Y. Ohzawa, H. Iwata, J. Fluorine Chem. 112 (2001) 233.
[6] T. Nakajima, V. Gupta, Y. Ohzawa, H. Iwata, A. Tressaud, E. Durand, J. Fluorine Chem. 114 (2002) 209.
[7] T. Nakajima, V. Gupta, Y. Ohzawa, M. Koh, R.N. Singh, A. Tressaud, E. Durand, J. Power Sources 104 (2002) 108.
[8] T. Nakajima, V. Gupta, Y. Ohzawa, H. Iwata, A. Tressaud, E. Durand, Mol. Cryst. Liq. Cryst. 388 (517) (2002) 103.
[9] R. Takagi, T. Okubo, K. Sekine, T. Takamura, Denki Kagaku 65 (1997) 333.
[10] M. Yoshio, H. Wang, K. Fukuda, Y. Hara, Y. Adachi, J. Electrochem. Soc. 147 (2000) 1245.
[11] H. Wang, M. Yoshio, T. Abe, Z. Ogumi, J. Electrochem. Soc. 149 (2002) A499.
[12] M. Yoshio, H. Wang, K. Fukuda, T. Umeno, N. Dimov, Z. Ogumi, J. Electrochem. Soc. 149 (2002) A1598.
[13] Y.-S. Han, J.-Y. Lee, Electrochim. Acta 48 (2003) 1023.
[14] Y. Ohzawa, M. Mitani, T. Suzuki, V. Gupta, T. Nakajima, J. Power Sources 122 (2003) 153.
[15] T. Nakajima, in: T. Nakajima (Ed.), Fluorine–Carbon and Fluoride–Carbon Materials—Chemistry, Physics and Applications, Marcel Dekker, New York, USA, 1995 (Chapter 1).
[16] T. Nakajima, N. Watanabe, in: Graphite Fluorides and Carbon–Fluorine Compounds, CRC Press, Boca Raton, USA, 1991 (Chapter 6).
[17] T. Nakajima, A. Mabuchi, R. Hagiwara, N. Watanabe, F. Nakamura, J. Electrochem. Soc. 135 (1988) 273.
[18] R. Fong, U. von Sacken, J.R. Dahn, J. Electrochem. Soc. 137 (1990) 2009.
[19] M. Inaba, S.-K. Jeong, T. Abe, Z. Ogumi, Battery Technol. 13 (2001) 39.
[20] M. Inaba, Y. Kawatate, A. Funabiki, S.-K. Jeong, T. Abe, Z. Ogumi, Electrochim. Acta 45 (1999) 99.
[21] N. Watanabe, T. Nakajima, R. Hagiwara, J. Power Sources 20 (1987) 87.
[22] T. Fukutsuka, S. Hasegawa, Y. Matsuo, Y. Sugie, T. Abe, Z. Ogumi, Abstract of the 26th Fluorine Conference of Japan, Fukui, 14–15 November 2002, pp. 162–163.
[23] H. Fujimoto, A. Mabuchi, K. Tokumitsu, T. Kasuh, Carbon 38 (2000) 871.
[24] K. Moriguchi, S. Munetoh, M. Abe, M. Yonemura, K. Kamei, A. Shintani, A. Omaru, M. Nagamine, J. Appl. Phys. 88 (2000) 6369.