Surface Fluorination and Oxidation of Carbon Materials for Negative Electrode of Lithium Ion Secondary Battery

Tsuyoshi Nakajima* and Katsunori Yanagida

Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto, 606-01, Japan

The effect of surface modification of carbon materials on their electrochemical behavior has been studied. Fluorination, ozonization and air-oxidation of carbon surfaces increased the charge-discharge capacities. The change in the d-spacings of carbon materials due to surface modification was negligibly small. XPS measurement indicated that surface oxygen contents slightly increased not only in oxidized samples but also in fluorinated one. XPS also revealed the existence of nearly ionic and semi-covalent fluorines at the surface of the fluorinated sample.

KEYWORDS : Surface fluorination, Surface oxidation, Carbon materials, Lithium secondary battery

1. Introduction

Recently carbon materials are used as negative electrodes of lithium ion secondary battery to avoid the dendrite formation of lithium at negative electrode. Characteristics of carbon materials as negative electrodes would be governed by such factors as (1) crystallinity1), (2) surface area, (3) change of electronic structures of carbon materials by replacing some carbon atoms with boron or nitrogen atoms2)-3) and (4) change of chemical interaction with lithium ion by doping of a foreign element4). Concerning the surface of a carbon material, the electrochemical behavior seems to be influenced not only by surface area but also by surface microstructure and surface functional groups interacting with lithium ions. It was recently reported that air-oxidation of carbon materials at high temperatures significantly improved the electrochemical characteristics such as capacities, cycling behaviors and so on5)-7). Oxidation of carbon materials would give rise to the enlargement of surface area, the increase in carboxylic and hydroxylic groups at the surface, and the change of surface microstructure5)-7). Among a large number of graphite intercalation compounds (GICs), only two GICs, graphite fluorides and graphite oxide have covalent bondings between host graphite and intercalated species. These GICs have, however, quite different surface properties : graphite fluorides are hydrophobic whereas graphite oxide is hydrophilic8). In addition to hydrophobic graphite fluorides, (CF)n and (C2F)n, which are prepared by high temperature direct fluorination of carbon materials, there exist other fluorine-graphite intercalation compounds, CxFs synthesized at temperatures below 100°C in the presence of a Lewis acid such as HF8)-9). The latter CxFs have ionic to semi-covalent C-F bonding, that is, hydrophilic nature8),9). Taking into account the chemical bonds and surface properties of these compounds, we have made surface fluorination and oxidation of carbon materials and examined the effect of the surface modification on the electrochemical behaviors.

2. Experimental

Carbon materials used in this study were natural graphite powder (diameter : ca. 7μm) and carbon nanotube heat-treated at 3000°C. The carbon nanotube was prepared by arc-discharge of graphite rod under the con-
ditions, 22-34 V and 60 A. TEM observation indicated that the carbon nanotube prepared consisted of nanotubes with outer and internal diameters of 15-30 nm and 5-8 nm, respectively and small carbon particles with diameters of 30-90 nm.

Surface modification of carbon materials was made by three different methods: fluorination by elemental fluorine, ozonization and air-oxidation. The surface fluorination was performed at 120 °C by fluorine gas of $0.2 \times 10^5$ Pa for 2 min (F$_2$ supplied by Daikin Industries, Ltd.). The surface oxidation was made by oxygen gas flow containing 1 vol. % ozone at 100 mlmin$^{-1}$ for 5 h at ambient temperature, and by air-treatment at 700 °C for 15 min.

Surface-modified carbon materials were analyzed by elemental analysis of carbon, oxygen and fluorine, X-ray diffractometry and XPS. XPS measurements were performed on carbon, oxygen and fluorine using Ulvac Phi Model 5500 spectrometer. The binding energies were determined relative to that of C$_{1s}$ electron of graphite, 284.3 eV without charging correction.

Electrode preparation and electrochemical measurements were made in the following manners. The working electrode (diameter: 9 mm, thickness: 0.1-0.2 mm) was prepared by pressing a mixture of carbon material (4.5 mg) and polyvinylidene fluoride (0.36-0.45 mg) into a pellet covered with a filter paper at one side under 200 kgcm$^{-2}$. The electrochemical cell used in this study consisted of the working electrode (positive electrode), lithium negative electrode and lithium reference electrode in 1 M LiClO$_4$-EC / DEC (1:1) solution supplied by Mitsubishi Chemical Corporation. The electrochemical characteristics of surface-modified carbon materials were evaluated by cyclic voltammetry at a scan rate of 0.2 mVs$^{-1}$ and charge-discharge cycling at an apparent current density of 0.1 mAcm$^{-2}$ at 20 °C.

3. Results and Discussion

3.1 Surface modification of carbon materials by fluorination and oxidation

No fluorine and oxygen were detected by elemental analysis in all the surface-modified samples. From the sensitiveness of the analytical methods, the fluorine and oxygen contents are estimated to be less than 0.3 wt %. The d (001) value of carbon nanotube was decreased from 0.341 nm to 0.337 nm by heat-treatment at 3000 °C.

<table>
<thead>
<tr>
<th>Method</th>
<th>d (001) (nm)</th>
<th>d (002) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.337</td>
<td>0.336</td>
</tr>
<tr>
<td>Ozonization</td>
<td>0.339</td>
<td>0.337</td>
</tr>
<tr>
<td>Fluorination</td>
<td>0.338</td>
<td>0.338</td>
</tr>
<tr>
<td>Air-oxidation</td>
<td>0.338</td>
<td>0.336</td>
</tr>
</tbody>
</table>

a) Corresponding to d (002) diffraction line of graphite.

Since graphene layers do not take ABAB····· stacking in carbon nanotube, the diffraction line corresponding to (002) line of graphite should be indexed as (001). X-ray diffraction measurement revealed that surface modification gave rise to only negligible change in d (001) and d (002) values and half widths of the same diffraction lines. The d (001) and d (002) values of pristine and surface-modified samples are given in Table 1, which indicates that the increase in the d (001) and d (002) values by surface modification is negligibly small. The results obtained by X-ray diffraction shows that high crystallinity of carbon materials is still kept after surface modification.

XPS reveals the surface elements, chemical bondings and surface compositions of solids. Fig.1 shows C$_{1s}$, O$_{1s}$ and F$_{1s}$ spectra of heat-treated carbon nanotube and surface-modified ones. The C$_{1s}$ spectra exhibited their peaks at 284.3-284.4 eV. The O$_{1s}$ spectra were also similar to each other, consisting of two contributions due to carbonyl (530.7-531.1 eV) and hydroxyl (532.4-532.6 eV) groups. The F$_{1s}$ spectrum of the fluorinated sample had two peaks at 685.0 and 687.7 eV, which indicate nearly ionically and semi-covalently bonded fluorines, respectively. Table 2 lists the surface compositions of carbon nanotube and surface-modified ones, calculated from the peak areas of XPS spectra. The O$_{1s}$ spectra may include the contribution due to adsorbed water molecules at ca. 535 eV in addition to carbonyl and hydroxyl groups existing at the sample surfaces. Though the amounts of oxygen species were less than 3 % in all the samples as listed in Table 2, the surface-modified samples had higher oxygen contents than the pristine sample. Especially the ozonized sample possessed the highest oxygen content. Even in the fluorinated sample, a larger amount of oxygen was detected than that of fluorine. A part of oxygen species detected may have
Fig. 1 XPS spectra of heat-treated carbon nanotube and the surface-modified ones.

a) pristine sample, b) ozonized sample, c) fluorinated sample, d) air-oxidized sample.

Table 2 Surface compositions of carbon nanotube and surface-modified samples, calculated from the peak areas of XPS spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (%)</th>
<th>O (%)</th>
<th>F (%)</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine sample</td>
<td>98.7</td>
<td>1.3</td>
<td>—</td>
<td>0.013</td>
</tr>
<tr>
<td>Ozonized sample</td>
<td>97.4</td>
<td>2.6</td>
<td>—</td>
<td>0.027</td>
</tr>
<tr>
<td>Fluorinated sample</td>
<td>97.8</td>
<td>1.5</td>
<td>0.7</td>
<td>0.015</td>
</tr>
<tr>
<td>Air-oxidized sample</td>
<td>98.4</td>
<td>1.6</td>
<td>—</td>
<td>0.016</td>
</tr>
</tbody>
</table>
been generated from the reaction of adsorbed fluorine atoms with moisture.

3.2 Electrochemical characteristics of surface-modified carbon materials

As-prepared carbon nanotube exhibited the similar charge-discharge curves as natural graphite, however, the capacity was about 80% of that of natural graphite. Heat-treatment at 3000°C increased the capacity to the same value as that of natural graphite.

Figs. 2 and 3 show the cyclic voltammograms at 1st cycle for heat-treated carbon nanotube and natural graphite with their surface-modified samples, respectively. No reduction currents were observed at around 3 V in all the samples because of the negligible amounts of surface oxygen and fluorine species. The reduction current at 0.63-0.65 V is due to the reduction of organic solvents, being observed only at 1st cycle. It is also obvious from the figures that the reduction currents at 0 V and oxidation peak currents are significantly increased by surface modification in both carbon materials. The reduction currents at 0 V increased from 307 mA g⁻¹ (Fig. 2A) to 353 mA g⁻¹ (Fig. 2B), 429 mA g⁻¹ (Fig. 2C) and 400 mA g⁻¹ (Fig. 2D), and oxidation peak currents also increased from 207 mA g⁻¹ (Fig. 2A) to 256 mA g⁻¹ (Fig. 2B), 328 mA g⁻¹ (Fig. 2C) and 326 mA g⁻¹ (Fig. 2D) by ozonization, fluorination, and air-oxidation, respectively. According to the increase in the currents, the oxidation peaks were observed at slightly lower potentials, 0.27 V (Fig. 2B), 0.24 V (Fig. 2C) and 0.27 V (Fig. 2D) while that of the pristine nanotube was situated at 0.29 V (Fig. 2A). The effect of surface modification is similar in case of natural graphite as shown in Fig. 3. The reduction currents at 0 V increased from 128 mA g⁻¹ (Fig. 3A) to 172 mA g⁻¹ (Fig.

![Fig.2 Cyclic voltammograms for heat-treated carbon nanotube and surface-modified samples (0.2 mVs⁻¹, 1st cycle)](image)

A : heat-treated carbon nanotube, B : ozonized sample, C : fluorinated sample, D : air-oxidized sample.
3B), 187 mAg⁻¹ (Fig. 3C) and 172 mAg⁻¹ (Fig. 3D), and oxidation peak currents increased from 81 mAg⁻¹ (Fig. 3A) to 108 mAg⁻¹ (Fig. 3B), 139 mAg⁻¹ (Fig. 3C) and 118 mAg⁻¹ (Fig. 3D). The oxidation peaks were observed at 0.25 V (Fig. 3B), 0.25 V (Fig. 3C) and 0.23 V (Fig. 3D) in comparison with 0.28 V for the pristine sample (Fig. 3A). Thus the larger currents were observed for carbon nanotube than natural graphite in any case. Intercalation and deintercalation of lithium ion would be easier in carbon nanotube because carbon nanotube used in this study consists of 15 to 32 graphene layers with carbon particles having large surface areas.

Fig. 3 Cyclic voltammograms for natural graphite and surface-modified samples (0.2 mVs⁻¹, 1st cycle). A: natural graphite, B: ozonized sample, C: fluorinated sample, D: air-oxidized sample.

Fig. 4 Charge-discharge curves for heat-treated carbon nanotube and the surface-modified samples (0.1 mAcm⁻², 2nd cycle). a) pristine sample, b) ozonized sample, c) fluorinated sample, d) air-oxidized sample.

Fig. 5 Charge-discharge curves for natural graphite and the surface-modified samples (0.1 mAcm⁻², 2nd cycle). a) pristine sample, b) ozonized sample, c) fluorinated sample, d) air-oxidized sample.
Figs. 4 and 5 show charge-discharge curves at 2nd cycle for pristine and surface-modified samples. The feature of current-voltage curves for carbon nanotube samples in Fig. 4 are similar to those for natural graphite samples in Fig. 5. In both carbon materials, the surface-modified samples always exhibited higher capacities than the pristine carbons during 7 to 10 cycles examined. The increments in the capacities were 4%, 5% and 9% at 10th cycle for the ozonized, fluorinated and air-oxidized carbon nanotubes, respectively. Those for surface-modified natural graphites were 8%, 9% and 17% at 7th cycle in the same order of the samples. The relative differences in the charge capacities were not largely different even when the cycle number increased. The coulombic efficiencies increased with increasing cycle number, approaching 90% after 5th cycle. No distinct difference in the coulombic efficiencies was found among pristine and surface-modified samples.

The data obtained in the present study indicate that the surface fluorination and oxidation improve the electrochemical behaviors of carbon materials, however, it cannot be concluded which one of the surface modification methods is the best because it is not known for the moment whether the data presented here were obtained under optimum conditions or not. The main effect caused by surface modification would be the increase in the moderate chemical interaction of oxygen and fluorine species with lithium ions. Since the current density was small in the present study, the enlargement of surface area by surface modification probably gave the negligible effect to the capacity increase. It is already pointed out that highly oxidized carbon materials show larger irreversible capacities and lower cycleabilities than less oxidized one. The optimum concentrations in the surface oxygen and fluorine would exist. The fluorinated sample has nearly ionic and semi-covalent C-F bonds at the surface as shown in Fig. 1. Fluorinated graphite containing nearly ionic and semi-covalent fluorines has higher hydrophilicity than that having covalent C-F bonds and graphite itself. This property may provide the carbon materials with easier chemical interaction with lithium ions.

References