Effects of the chemical etching of single-walled carbon nanotubes on their lithium storage properties

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1. Introduction

Carbon nanotubes (CNTs), multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) are synthesized by various techniques including arc-discharge, laser ablation, and chemical-vapor deposition (CVD) [1,2]. Recently, it has been reported that SWCNTs of high quality, large scale, and low cost can be synthesized on supported catalysts by thermal CVD [3–5]. A number of purification methods have been developed to increase the quality and yield of CNTs [6–8]. They can be categorized into four major methods: liquid-phase oxidation, gas-phase oxidation, filtration, and chromatography. The gas-phase oxidation was reported to be very effective purification method for SWCNTs synthesized on supported catalysts by thermal CVD.

CNTs with a 1D host lattice structure have been received much attention as the Li storage host materials for high energy density Li-ion rechargeable batteries. Because the Li storage properties of CNTs are closely related to their structure and morphology, the various treatments have been used to improve their Li storage properties. As a result, SWCNTs [9–14] show better performance than MWCNTs [15–20] as the host materials for Li-ion batteries. According to the first-principles calculations, energetically the inner core of SWCNTs is as favorable as Li insertion sites, and these treatments modify the structure of SWCNTs by introducing lateral defects on the surface of SWCNTs and also by shortening the length of SWCNTs, and hence leading to the increase in the Li storage capacity. The surface functional groups of SWCNTs formed by these treatments appears to change the nature of solid electrolyte interface (SEI) formed by reaction of those with Li, and also the nature of SEI has an effect on the Li storage capacit-
ity. However, the exact effects of the structural characteristics and the surface functional groups of SWCNTs by these treatments on the Li storage properties of SWCNTs are not yet reported clearly.

In this paper, the structural characteristics and the surface functional groups of SWCNTs changed by the purification and the chemical etching process have been investigated to determine their effects on the Li storage properties of SWCNTs.

2. Experimental

2.1. Purification and chemical etching of SWCNTs

The SWCNTs were synthesized on Al2O3 aerogel supported Fe/Mo catalysts by thermal CVD [4,5]. The raw products of SWCNTs consisted of mainly SWCNTs and impurities such as the support, catalyst particles and small amount of amorphous carbon mostly coated on the catalyst particles. They were purified [5] by stirring in 1:3 ratio of concentrated HF acid (50%) and distilled water for 18 h to dissolve the support particles, and then followed by gas-phase oxidation in a 15% air/Ar mixture at 550 °C for 1 h to burn the amorphous carbon coated on the catalyst particles. Further, the oxidized SWCNTs were sonicated in concentrated HCl acid (37%) for 10 min to dissolve the metal oxides formed and the catalyst particles exposed by the gas-phase oxidation. These purified samples were filtered to remove the acid for several times, and dried at 150 °C for 12 h. The purified SWCNTs were chemically etched by sonication in 3:1 ratio of concentrated H2SO4 acid (96%) and HNO3 acid (70%) solution for 5–20 h. The etched samples were also filtrated and dried in the same condition of the purified samples. All the samples were dried again at 150 °C for 5 h in 5 × 10−6 torr vacuum before using.

2.2. Electrochemical test of Li/SWCNT cells

The charge/discharge test of Li/SWCNT cells was performed under a galvanostatic mode using WBCS 3000 (WonATech©) system. The cells were discharged (insertion) and charged (extraction) under galvanostatic mode at a constant current of 50 mA per SWCNT weight between 0 and 3 V. The charge/discharge characteristics for several samples, taken from different batches were measured under the same conditions, showed a small deviation values of capacities in the range of ±30 mAh g−1. The electrochemical impedance spectroscopy (EIS) measurement was carried out using FRA2 and PGSTAT20 system (Autolab©) over the frequency range 100 kHz to 0.01 Hz. The two-electrode cell for the charge/discharge test consisted of Li foil as an anode and SWCNT film as a cathode. The three-electrode cell for the EIS measurement consisted of Li foil as reference and counter electrodes and SWCNT film as working electrode. The SWCNT electrodes were prepared by coating slurries consisting of SWCNTs (85 wt.%) with acetylene carbon black (5 wt.%) and poly(vinylidene fluoride) (PVdF) (10 wt.%) as a binder dissolved in 1-methyle-2-pyrrolidinone (NMP) solution on stainless steel substrate. All the SWCNT electrodes were dried for 5 h at 150 °C in 5 × 10−6 torr vacuum. After drying, the weight of each sample was measured to be about 2–4 mg. The Li/SWCNT cells were assembled using coin type cell for the charge/discharge test and Swagelok three-electrode T-cell for the EIS measurement in an Ar filled glove box. A polypropylene filter soaked with liquid electrolyte (Merck©) which was 1 M of LiPF6 dissolved in 1:1 volume ratio of ethylene carbonate (EC) and dimethyl carbonate (DMC) was placed between anode and cathode in the cell.

3. Results and discussion

3.1. Structure characteristics of purified and etched SWCNTs

Fig. 1 shows the transmission electron microscopy (TEM) images of the raw SWCNTs and the purified SWCNTs. TEM images indicate that SWCNTs were synthesized with a bundle type successfully on supported catalysts by thermal CVD and the impurities of the raw SWCNTs were the support, catalyst particles and small amount of amorphous carbon mostly coated on the catalyst particles, as shown in Fig. 1(a). The impurities were effectively removed by the purification process of an acidic treatment followed by the gas-phase oxidation, as shown in Fig. 1(b). The final purified products consisted of 95% SWCNTs with 10 μm in length and 30–50 nm in bundle diameter.

The results of thermal gravimetric analysis (TGA) and inductively coupled plasma (ICP) analysis show that the amount of residual catalysts in the purified SWCNTs decreased to a negligible level with the purification process, as shown in Fig. 2 and Table 1. Most of the support particles were removed by stirring in diluted HF acid, and the amorphous carbon coated on the catalyst particles was burned during the gas-phase oxidation. The metal oxides formed during the gas-phase oxidation and the catalyst particles remained were removed by sonication in concentrated HCl acid.

![Fig. 1. TEM images (a) of the raw SWCNTs synthesized on supported catalysts by thermal CVD and (b) the purified SWCNTs by an acidic treatment followed by the gas-phase oxidation.](image)

![Fig. 2. TGA plots of the raw SWCNTs and the purified SWCNTs under an air flow at a ramp rate of 5 °C min−1.](image)

<table>
<thead>
<tr>
<th></th>
<th>Al2O3 (wt.%)</th>
<th>Fe (wt.%)</th>
<th>Mo (wt.%)</th>
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<tbody>
<tr>
<td>Raw SWCNTs</td>
<td>27.5</td>
<td>1.87</td>
<td>0.78</td>
</tr>
<tr>
<td>Purified SWCNTs</td>
<td>0.13</td>
<td>0.66</td>
<td>0.09</td>
</tr>
<tr>
<td>Etched SWCNTs for 10h</td>
<td>0.07</td>
<td>0.12</td>
<td>0.02</td>
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The SWCNTs were almost unaffected by the gas-phase oxidation because of higher thermal stability of SWCNTs than the amorphous carbon against the oxidation [5].

Fig. 3 shows TEM images of the chemically etched SWCNTs, demonstrating that the average length of SWCNTs reduced to about 1 and 0.2 μm and the average diameter of SWCNT bundles also reduced to about 20 and 10 nm after the chemical etching for 10 and 20 h, respectively. It is believed that the lateral defects, such as micro-cavities or nano-voids on the surface and opened ends of the etched SWCNTs increased with the etching time, because the surface of SWCNTs was affected easily by the chemical etching.

### 3.2. Charge/discharge characteristics of purified and etched SWCNTs

The charge/discharge characteristics for insertion/extraction of Li ions into/from the purified SWCNTs and the etched SWCNTs are shown in Fig. 4(a). The reversible capacity \( C_{\text{rev}} \) is defined as the first charge capacity while the irreversible capacity \( C_{\text{irr}} \) is defined as the difference between the first discharge and charge capacities. The change in \( C_{\text{rev}} \) and \( C_{\text{irr}} \) of the etched SWCNTs is given in Fig. 4(b) as a function of the etching time. For the purified SWCNTs, the \( C_{\text{rev}} \) is 616 mAh g\(^{-1}\) (Li\(_{1.7}C_6\)) whereas the \( C_{\text{irr}} \) is 1573 mAh g\(^{-1}\) (Li\(_{4.2}C_6\)) that is very higher than the \( C_{\text{rev}} \). The \( C_{\text{rev}} \) of the etched SWCNTs increases with the etching time to 878 mAh g\(^{-1}\) (Li\(_{2.4}C_6\)) after etching for 10 h, while, after further etching for 20 h, the \( C_{\text{rev}} \) decreases slightly to 794 mAh g\(^{-1}\) (Li\(_{2.1}C_6\)). On the other hand, the \( C_{\text{irr}} \) increases continuously with the etching time to 1772 mAh g\(^{-1}\) (Li\(_{4.8}C_6\)) after etching for 20 h. Therefore, the coulombic efficiency of the etched SWCNTs increases with the etching time from 28% for the purified SWCNTs to 34% after etching for 10 h, while, after further etching for 20 h, the coulombic efficiency decreases slightly to 31%.

Differential capacity \( \frac{dQ}{dV} \) curves drawn using the data in Fig. 4(a) are presented in Fig. 5. The \( \frac{dQ}{dV} \) curves for all the samples clearly show peaks that correspond to the insertion/extraction of Li ions. Peak at 0.8 V appear in the first discharge \( \frac{dQ}{dV} \) curve of the purified SWCNTs (Fig. 5(a)) and correspond to the voltage plateau at 0.8 V in the first discharge curve shown in Fig. 4(a). These are presumably due to an irreversible reaction for the for-
formation of solid electrolyte interface (SEI) in the Li insertion into the SWCNTs [16,17]. However, the peak around 0.8 V in the first discharge \(dQ/dV\) curve of the etched SWCNTs was not observed, indicating that the surface film different from well-known SEI was formed on the etched SWCNTs. It is evident for the etched SWCNTs in Fig. 4(a) that the decrease in the initial voltage to 0.8–0.25 V in the first discharge appears to be associated with the reduction reaction of the surface functional groups in the SWCNTs with Li ions [17–19]. The surface functional groups of the SWCNTs contain \(\text{C} = \text{O}\) (1500–1680 cm\(^{-1}\)) and C–H (2920 cm\(^{-1}\)) bonds as confirmed in the Fourier transform infrared (FT-IR) spectra for the purified SWCNTs and the etched SWCNTs, as shown in Fig. 6. It is evident from the change in peak intensity associated with each bond in Fig. 6 that an amount of the surface functional groups formed on the SWCNTs increases with the etching time. These \(\text{C} = \text{O}\) and C–H bonds were found to be carbonyl \((\text{C} = \text{O})\) and carboxyl \((\text{C} \text{–COOH})\) groups [20,23,24]. The surface functional groups formed on the SWCNTs during the chemical etching appears to be converted into the surface Li carboxylic salt \((\text{–COOLi})\) and/or surface –OLi groups by the reduction reaction of the surface functional groups with Li ions at the initial stage of the first discharge. It is believed that these surface Li carboxylic salt \((\text{–COOLi})\) and/or surface –OLi groups on the etched SWCNTs reduce to the \(\text{Li}_2\text{CO}_3\)-based SEI formed by decomposition of EC-, diethyl carbonate (DEC)-, DMC-, or propylene carbonate (PC)-based electrolytes [20,23,24].

In the first discharge \(dQ/dV\) curves (Fig. 5(a)), the discharge current area below 0.25 V for the etched SWCNTs is larger than that for the purified SWCNTs. This suggests that more Li ions are inserted into the etched SWCNTs below 0.25 V. It is expected that the Li ions were inserted into the inner core of the etched SWCNTs through the opened ends formed by the chemical etching of SWCNT bundles [11]. It appears that the insertion of Li ions into the inner core of the etched SWCNTs was facilitated more than that of the purified SWCNTs due to the opened ends and the shortened length of the etched SWCNTs.

In the first charge \(dQ/dV\) curves (Fig. 5(b)), the peaks around 1.25 and 2.25 V are observed for the purified SWCNTs and the peaks around 1.75 and 2.25 V are observed for the etched SWCNTs. For the etched SWCNTs, the peak around 1.25 V for the purified SWCNTs shifts to 1.75 V. It is believed that the peak around 1.25 V was attributed to the extraction of Li ions from the inner core of SWCNTs [12]. The extraction of Li ions from the inner core of the etched SWCNTs appears to be easier than in the case of the purified SWCNTs due to the opened end and the shortened length of the etched SWCNTs. Also, the peak around 2.25 V was attributed to the extraction of Li ions bonded to the surface functional groups in SWCNTs [12]. An amount of the extracted Li ions from the surface functional groups in the etched SWCNTs is larger than that in the purified SWCNTs due to increase in the surface functional groups by the chemical etching.

It is evident from the large voltage hysteresis in the charge/discharge curve shown in Fig. 4(a) that most of the Li ions were inserted below 0.25 V in the discharge, but extracted broadly between 0 and 3 V. This means that the extraction of Li ions from both the purified SWCNTs and the etched SWCNTs was greatly hindered. Such a large hysteresis was previously observed for SWCNTs [9–14] and MWCNTs [15–20], and for ball-milled sugar carbons [25] and soft carbons containing substantial hydrogen [26]. This feature is generally attributed to bonding changes in the host, or activated process such as the formation of C–H–Li [26] or C–O–Li [27] species. Because the surface functional groups formed on the etched SWCNTs increase with the etching time, the large voltage hysteresis was observed in the etched SWCNTs.

The exact mechanism for the enhanced \(C_{\text{rev}}\) in the etched SWCNTs compared with that in the purified SWCNTs was not yet clear. Several models have been reported to account for the excess \(C_{\text{rev}}\) observed in other carbonaceous materials, which include the formation of Li multi-layers and \(\text{Li}_2\) covalent molecules on graphene layers, the formation of C–H–Li bonds in soft carbons, filling of micro-cavities and adsorption of Li ions on both sides of isolated graphene layers [28]. The \(C_{\text{rev}}\) in thermally [29,30] and chemically [23,24] oxidized carbonaceous materials is enhanced by filling of Li ions onto the lateral defects, such as micro-cavities or nano-voids formed on the surface, doping of those at the edges of graphene layers, and reaction of those with the surface functional groups.
Solid-state $^7$Li MAS NMR spectra for the purified SWCNTs and the etched SWCNTs at 10 h at 0.01 V on the first discharge curves (Fig. 4(a)) are given in Fig. 7. In both samples, resonances near 0 ppm were detected only. There are no peaks neither of LiC$_6$ and LiC$_{12}$ which should be at −40–45 ppm nor metallic lithium at 265 ppm [31,32]. In the spectrum of the purified SWCNTs can see rather symmetric line at −2 ppm. Single line is also presented in the spectrum of the etched SWCNTs, but it slightly asymmetric with shoulder at positive value (−10 ppm) of chemical shifts. The signal at near 0 ppm with shoulder at 10 ppm is assignable to Li ions inserted in different sites of disordered carbon regions with weak interactions between Li ions and electrons in carbon layers. Covalently bonded Li ions can also appear near 0 ppm [31,32]. Therefore, the NMR spectra of the purified SWCNTs and the etched SWCNTs are not consistent with a “graphite-lithium-intercalation-compound” mechanism, but those are rather consistent with a nongraphitic-carbon-insertion mechanism (i.e., Li ions in the borders of graphene layers, in the external surface of nanoparticles, adsorbed in the surface of single graphene sheets, near defects sites, in nanocavities, and placed between disorderly stacked carbon sheets) [32]. For the etched SWCNTs, the edges of graphene layers, the lateral defects, and the surface functional groups are increased with the etching time. Also, the inner core of the etched SWCNTs is facilitated more than that of the purified SWCNTs due to the opened ends and the shortened length of the etched SWCNTs. Therefore, these factors of the etched SWCNTs facilitate the insertion of Li ions into the etched SWCNTs and enhance the $C_{rev}$ in the etched SWCNTs with large voltage hysteresis by hindrance of the extraction of Li ions from the etched SWCNTs. It is believed that the reduction of $C_{rev}$ in the etched SWCNTs for the further etching time is attributed to the increase in the disordered/amorphous carbon at the expense of the etched SWCNTs.

3.3. Electrochemical impedance behaviors of purified and etched SWCNTs

Nyquist plots of EIS for the purified SWCNTs and the etched SWCNTs for 10 h at 0.1 V on the first discharge curves (Fig. 4(a)) are given in Fig. 8. Two separated semicircles in the high and intermediate frequency range 100–0.01 kHz and a sloping line in the low frequency range 10–0.01 Hz are observed in the purified SWCNTs and the etched SWCNTs. The first semicircle at the high frequency corresponds to the migration of Li ions through the passivation film, such as the SEI and the second semicircle at the intermediate frequency corresponds to the charge transfer reaction, and the sloping line in the low frequency corresponds to the diffusion reaction as Warburg’s impedance [33,34].

The film resistance ($R_f$) of the etched SWCNTs at the high frequency is smaller than that of the purified SWCNTs. This indicates that the $R_f$ of the passivation film formed on the etched SWCNTs is smaller than that of the purified SWCNTs, although the surface area for formation of the passivation film, such as the SEI is increased obviously after the chemical etching. As mentioned above, the surface film different from well-known SEI was formed on the etched SWCNTs by the reduction reaction of the surface functional groups with Li ions. It is proved that the $R_f$ of the surface film on the etched SWCNTs by the surface functional groups is smaller than that of the SEI on the purified SWCNTs.

The charge transfer resistance ($R_c$) of the etched SWCNTs at the intermediate frequency is smaller than that of the purified SWCNTs, corresponding to the strong tendency for charge accumulation in the etched SWCNTs. The $R_c$ relates to the electronic resistance depending on the structure of CNTs [33,34]. For CNTs with the closed end structure, both ends of the tubes are capped by graphene layers with pentagons and heptagons, which have large electronic resistance. Once the tubes are open, the electronic resistance decreases with the absence of pentagons and heptagons, and also the inner core plays an important role in the charge accumulation. For the etched SWCNTs, the opened end and the shortened length structure result in the strong tendency for charge accumulation. Also, the surface functional groups contribute to the charge accumulation in the etched SWCNTs. It is believed that the Li ions accumulated in the inner core and the surface functional groups are extracted with the large voltage hysteresis by great hindrance in the etched SWCNTs.

3.4. Cycle life behaviors of purified and etched SWCNTs

Fig. 9 shows the reversible cycle capacity and the coulombic efficiency of the purified SWCNTs and the etched SWCNTs for 10 h as a function of the cycle number. In the cycle capacity curves shown in Fig. 9(a), the purified SWCNTs present almost uniform cycle capacity which slightly decreases, demonstrating that the purified SWCNTs maintain 85% (524 mAh g$^{-1}$) of their initial capacity (616 mAh g$^{-1}$) after 50 cycles. However, the etched SWCNTs maintain 70% (618 mAh g$^{-1}$) of their initial capacity (878 mAh g$^{-1}$) after 50 cycles, indicating that the etched SWCNTs are electrochemically and chemically unstable during the charge/discharge cycling.

The cycle characteristics of the purified SWCNTs and the etched SWCNTs for 10 h are presented in the coulombic efficiency in detail,
shown in Fig. 9(b). Coulombic efficiency of the purified SWCNTs and the etched SWCNTs reaches to about 99% after 10th cycles. This suggests that the irreversible reaction in both the purified SWCNTs and the etched SWCNTs, such as formation of the SEI, is occurred continuously until 10th cycles. After completing the irreversible reaction in the purified SWCNTs and the etched SWCNTs, the charge/discharge cycling is stabilized, shown in Fig. 9(a). It is believed that the Li ions inserted into the inner core, the lateral defects, and the surface functional groups of the etched SWCNTs are extracted easily during the initial charge/discharge cycling, but an amount of the extracted Li ions from the etched SWCNTs decreases due to the accumulation of Li ions in the inner core, the lateral defects, and the surface functional groups during the charge/discharge cycling.

4. Conclusions

The SWCNTs synthesized on Al2O3 aerogel supported Fe/Mo catalysts by thermal CVD are effectively purified by an acidic treatment followed by the gas-phase oxidation. The purified SWCNTs are chemically etched in an acid solution for modifying the structural characteristics and the surface functional groups of the purified SWCNTs.

The Crev of the etched SWCNTs increases with the etching time, from 616 mAh g−1 (Li1.7C6) for the purified SWCNTs to 878 mAh g−1 (Li2.4C6) after etching for 10 h, while, after further etching for 20 h, the Crev decreases slightly to 794 mAh g−1 (Li2.1C6). The Crev of the etched SWCNTs also increases continuously with the etching time, from 1573 mAh g−1 (Li4.2C6) for the purified SWCNTs to 1772 mAh g−1 (Li4.8C6) after etching for 20 h.

For the etched SWCNTs, the edges of graphene layers, the lateral defects, and the surface functional groups are increased with the etching time. Also, the inner core of the etched SWCNTs is facilitated more than that of the purified SWCNTs due to the opened ends and the shortened length. These factors of the etched SWCNTs facilitate the insertion of Li ions into the etched SWCNTs and enhance the Crev in the etched SWCNTs with the large voltage hysteresis by hindrance of the extraction of Li ions from the etched SWCNTs. The reduction of Crev in the etched SWCNTs for the further etching time is attributed to the increase in the disordered/amorphous carbon at the expense of the etched SWCNTs. During the charge/discharge cycling, the Li ions inserted into the etched SWCNTs are extracted easily at the initial stage of cycling, but an amount of the extracted Li ions from the etched SWCNTs decreases due to the accumulation of Li ions in the etched SWCNTs.

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