Lithium insertion into purified and etched multi-walled carbon nanotubes synthesized on supported catalysts by thermal CVD

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Abstract

The effects of chemical processing on Li insertion into multi-walled carbon nanotubes (MWNTs) are reported. MWNTs were synthesized on the supported catalysts by the thermal CVD method, purified and chemically etched. And then the purified MWNTs and the etched MWNTs were electrochemically inserted with Li. The reversible capacity increased with increase in the etching time from 351 mAh/g (Li0:9C6) for the purified MWNTs to 681 mAh/g (Li1:8C6) for the etched MWNTs. The irreversible capacity also increased with increase in the etching time from 1012 mAh/g (Li2:7C6) for the purified MWNTs to 1229 mAh/g (Li3:3C6) for the etched MWNTs. The structural and chemical modifications in the etched MWNTs facilitated an insertion of Li ions into the etched MWNTs and enhanced the reversible capacity, but the large surface area of the etched MWNTs induced the large irreversible capacity. The extraction of Li ions from the purified MWNTs and the etched MWNTs had a great hindrance.

Keywords: A. Carbon nanotubes; B. Chemical vapor deposition, Etching; C. X-ray diffraction; D. Electrochemical properties

1. Introduction

Carbon nanotubes (CNTs) are currently investigated for technological applications in areas including electron field emission, energy storage, nanodevice, and nanocomposite, because of their unique materials properties [1–3]. Two types of carbon nanotubes, multi-walled carbon nanotubes (MWNTs) and single-walled carbon nanotubes (SWNTs), are synthesized by techniques including arc-discharge, laser ablation, chemical vapor deposition (CVD) [3,4]. Recently, it has been reported [5–10] that CNTs of high quality, large scale, and low cost can be synthesized on the supported catalysts by thermal CVD. A number of purification methods have been developed to increase the quality and yield of CNTs [10–14]. They can be categorized into four major methods: liquid-phase oxidation, gas-phase oxidation, filtration, and chromatography. The gas-phase oxidation is reported to be a very effective purification method for the SWNTs synthesized on the supported catalysts by thermal CVD [10].

Graphite and carbonaceous materials are commercially used as an anode in Li-ion batteries. They have a theoretical specific energy capacity of 372 mAh/g, limited by the thermodynamic equilibrium saturation composition of LiC6 [15–17].

CNTs with a 1D host lattice structure have been received much attention as a Li insertion host material in a high energy density Li-ion rechargeable battery. MWNTs prepared by various synthesis conditions [18–20] and thermal oxidation treatments [21–23] have exhibited a reversible capacities of 80–640 mAh/g (Li0:2C6 ∼ Li1:7C6). The Li reversible capacities of the raw SWNTs and the purified SWNTs were reported to be 450–600 mAh/g (Li1:5C6 ∼ Li1:6C6) [24,25], and increased to 790 and 1000 mAh/g (Li2:3C6 and Li2:7C6) by either mechanical ball-milling [26] or chemical etching [27,28]. It was reported that these treatments result in change in the structural characteristics and the surface functional groups of CNTs. These treatments modify
the structure of CNTs by introducing lateral defects on the surface of CNTs and also by shortening the length of CNT, and hence leading to the increase in the Li insertion capacity. The surface functional groups of CNTs formed by these treatments appear to change the nature of a solid electrolyte interface (SEI) formed by reaction of those with Li, and also the nature of the SEI has an effect on the Li insertion capacity. However, the exact effects of the structural characteristics and the surface functional groups of CNTs by these treatments on the Li insertion into CNTs are not yet reported clearly.

In this paper, we investigated the structural characteristics and the surface functional groups of MWNTs changed by the purification process and the chemical etching process, and then elucidated the effects of those on the Li insertion into MWNTs.

2. Experimental

2.1. Purification and etching of MWNTs

MWNTs were synthesized on the supported catalysts by thermal CVD. The raw products of MWNTs consisted of mainly MWNTs and impurities such as the support, catalyst particles and small amount of amorphous carbon mostly coated on the catalyst particles. They were purified [10] 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 MWNTs 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 MWNTs were chemically etched by sonication in 3:1 ratio of concentrated H₂SO₄ acid (96%) and HNO₃ acid (70%) solution [27–30] 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. Chargedischarge test of purified MWNTs and etched MWNTs

The charge/discharge test of Li/MWNTs cells was performed under a galvanostatic mode using MacPile II (Biologic®) system. The cells for the charge/discharge test consisted of Li foil as an anode and MWNTs film as a cathode. The MWNTs electrodes were prepared by coating slurries consisting of MWNTs (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 MWNTs 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/MWNT cells were assembled using Swagelok type cell 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 of purified MWNTs and etched MWNTs

Fig. 1 shows the transmission electron microscopy (TEM) images of the raw MWNTs and the purified MWNTs. The TEM images indicate that the impurities of the raw MWNTs were the support, catalyst particles and small amount of amorphous carbon 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 a gas-phase oxidation process, as shown in Fig. 1(b). The final purified products consisted of 95% MWNTs with over 10 μm in length and 10–20 nm in diameter. The results of thermal gravimetric analysis (TGA) and burning test also show that the contents of residual catalysts in the purified MWNTs decreased to a negligible level with the purification processes, as shown in Fig. 2. 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 process. Metal oxides formed during the gas-phase oxidation process and the catalyst particles remained were removed by sonication in concentrated HCl acid. MWNTs were almost unaffected by the gas-phase oxidation process because of higher thermal stability of MWNTs than the amorphous carbon against the oxidation [10,21–23]. However, some lateral defects, such as micro-cavities or nanovoids, on the surface of the purified MWNTs formed by the gas-phase oxidation process, as shown in Fig. 1(c). Most of ends in the purified MWNTs contacted with the catalyst particles were opened after the purification process, as shown in Fig. 1(d).

Fig. 3 shows TEM images of the chemically etched MWNTs, demonstrating that the average length of MWNTs reduced to about 2 and 0.2 μm after the chemical etching for 5 and 20 h, respectively. The number of lateral defects and opened ends of the etched
MWNTs increased with increasing the etching time, because the surface of MWNTs was affected easily by the chemical etching, as shown in Fig. 3(d).

Raman spectra for the purified MWNTs and the etched MWNTs were presented in Fig. 4 in which Raman-active vibration modes associated with MWNTs and disordered carbon were observed in all the samples. The ratio of total integrated intensity of the disordered carbon mode (around 1350 cm\(^{-1}\)) to that of the MWNTs mode (around 1600 cm\(^{-1}\)) increased with increasing the etching time. This indicates that the chemical etching process resulted in a significant increase in the intensity of the disordered carbon mode with broadening of the MWNTs peak, suggesting that MWNTs were converted to disordered/amorphous carbon by the chemical etching.

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

Fig. 5 shows the charge/discharge characteristics for insertion and extraction of Li ions into/from the purified MWNTs and also the etched MWNTs. The reversible capacity (\(C_{\text{rev}}\)) was defined as the first charge capacity while the irreversible capacity (\(C_{\text{irr}}\)) was defined as the difference between the first discharge and charge capacities. For the purified MWNTs, the \(C_{\text{rev}}\) is 351 mAh/g (Li\(_{0.9}\)C\(_6\)), whereas the \(C_{\text{irr}}\) is 1012 mAh/g (Li\(_{2.7}\)C\(_6\)) that is very high when compared with the \(C_{\text{rev}}\). The \(C_{\text{rev}}\) of the etched MWNTs increased with increasing etching time, from 351 mAh/g (Li\(_{0.9}\)C\(_6\)) for the purified MWNTs to 681 mAh/g (Li\(_{1.8}\)C\(_6\)) after etching for 10 h, while, after further etching for 20 h, the \(C_{\text{rev}}\) decreased slightly to 597 mAh/g (Li\(_{1.6}\)C\(_6\)). The \(C_{\text{irr}}\) also increased with increasing the etching time from 1012 mAh/g (Li\(_{2.7}\)C\(_6\)) for the purified MWNTs to 1229 mAh/g (Li\(_{3.3}\)C\(_6\)) after etching for 20 h. 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.

The initial voltage for the purified MWNTs in Fig. 5(a) decreased rapidly to 0.8 V when a current was applied to insert Li in the first discharge. However, for the etched MWNTs, the voltage decreased slowly to 0.8 V as the etching time increased, as shown in Fig. 5(b)–(d). The decrease in the initial voltage to 0.8 V in the first discharge process appears to be associated with the reduction reaction of the surface functional groups of MWNTs with Li ions [21]. The surface functional groups of MWNTs contained C=O and C–H bonds as confirmed in the Fourier transform infrared (FT-IR) spectra for the purified MWNTs and also the etched
MWNTs, as shown in Fig. 6. These C=O and C–H bonds were found to be carbonyl (C=O) and carboxyl (–COOH) groups [15,23,29–33]. It is evident from the change in the peak intensity associated with each bond in Fig. 6 that the amount of the surface functional groups formed on MWNTs increased with etching time. The contents of hydrogen and oxygen in the surface functional groups increased with increasing the etching time, as shown in Table 1. Thus, the slow decrease in the initial voltage to 0.8 V in the first discharge of the etched MWNTs is due to the reduction reaction of the surface functional groups with Li ions.

The surface functional groups formed on MWNTs during chemical etching appears to be converted into the surface Li carboxylic salt (–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 process. The Li2CO3-based SEI formed by decomposition of EC-, DEC-, DMC-, or PC-based electrolytes is chemically bonded to the surface Li carboxylic salt (–COOLi) and/or surface –OLi groups on the surface of MWNTs [23,32,33]. It is well known that the chemical bonded SEI (CB-SEI) acting as a molecular sieve reduces access of solvent molecules to the surface layer of carbonaceous materials, and hence reduces the amount of the C\text{irr} in the first insertion process with an increase in stability of carbonaceous electrode during further cycling [23,32,33].

The voltage plateau at 0.8 V appeared in the first discharge curves in Fig. 5 has been attributed to the formation of SEI on surface of MWNTs [15–17]. The voltage plateau at 0.8 V is proportional to the surface
area of MWNTs on which the SEI is formed. The voltage plateau in the first discharge curve for the purified MWNTs was observed more clearly than the one for the etched MWNTs.

Differential capacity \((dQ/dV)\) vs. voltage curves drawn using the data in Fig. 5 were presented in Fig. 7. The first discharge derivative curves of all the samples clearly showed peaks corresponding to insertion of Li ions, but no peak was observed in the second discharge derivative curves. The peak appeared in the first discharge derivative curve, corresponding to the voltage plateau in the discharge curve, is due presumably to an irreversible reaction in the Li insertion into MWNTs [22,31]. The peaks at 0.8 V for the etched MWNTs were more broadened compared with that for the purified MWNTs, indicating that the SEI was formed over wider range of discharge voltage in the etched MWNTs than in the purified MWNTs. In other words, the surface state of the etched MWNTs for the formation of SEI was less uniform and more broadened than that of the purified MWNTs due to lateral defects and opened ends formed during the chemical etching.

In the first discharge, the decomposition of electrolyte and the formation of SEI on the surface of MWNTs result in the large \(C_{ir}\) in MWNTs [19,21,22]. Since these factors are correlated with the large surface area of MWNTs, the large surface area is responsible for the large \(C_{ir}\) of MWNTs. The formation of lateral defects on the surface, opened ends, and the shortened length of the etched MWNTs resulted in increasing of the Brunauer–Emmett–Teller (BET) specific surface area of the etched MWNTs with increasing the etching time, as shown in Fig. 8. Therefore, the \(C_{ir}\) increased as a result of increasing the surface area of the etched MWNTs.

Following the voltage plateau at 0.8 V, the voltage declined with a sloping profile, and the majority of Li was inserted into MWNTs below 0.25 V. No voltage plateau was observed below 0.25 V in the charge/discharge curves, indicating the absence of a well defined insertion staging phenomena in the purified MWNTs and the etched MWNTs. The sloping profile of the voltage below 0.25 V is also observed in the amorphous carbonaceous materials [16,17].

It was reported on MWNTs of perfect structure with closed ends and that Li ions cannot be inserted between the graphene layers and into the inner core (the cavities in MWNTs’ center) through the carbon pentagons and hexagons. However, for MWNTs with opened ends and lateral defects, Li ions can be inserted between the graphene layers through the lateral defects [18] and the opened ends, and also inserted into the inner core through the opened ends [22]. In addition, Li ions are
doped onto the surface of MWNTs and also at the edges of graphene layers [16,17]. The insertion and extraction of Li ions between the graphene layers occurs reversibly, and proceed with a low voltage profile in the charge/discharge curves [15–17]. To examine the insertion of Li ions between the graphene layers of MWNTs, X-ray diffraction (XRD) experiments were performed on MWNTs at different voltage stage during the first discharge process, and the results are shown in Fig. 9. From the (002) diffraction peak at the open circuit voltage (OCV) for the purified MWNTs as well as the etched MWNTs, d(00 2) spacing or the distance between the graphene layers was calculated to be 3.44 Å using the Bragg’s equation. As the Li ions were inserted into the purified MWNTs and the etched MWNTs, the (00 2) diffraction peaks shifted slightly to lower angle, and hence the d(00 2) spacing of MWNTs discharged to 0 V

Table 1
The contents of hydrogen and oxygen consisted of the surface functional groups of the purified MWNTs and the etched MWNTs as a function of the etching time measured by the elemental analysis

<table>
<thead>
<tr>
<th>Hydrogen (at.%)</th>
<th>Oxygen (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified</td>
<td>4.9185</td>
</tr>
<tr>
<td>Etched for 5 h</td>
<td>8.4881</td>
</tr>
<tr>
<td>Etched for 10 h</td>
<td>8.5274</td>
</tr>
<tr>
<td>Etched for 20 h</td>
<td>9.5679</td>
</tr>
</tbody>
</table>

Fig. 6. FT-IR spectra in the absorbance mode of (a) the purified MWNTs and the etched MWNTs for (b) 5, (c) 10, and (d) 20 h.

Fig. 8. BET specific surface area of the purified MWNTs and the etched MWNTs as a function of the etching time measured using a N2 gas.
increased to 3.46 Å for the purified MWNTs and to 3.50 Å for the etched MWNTs. The slight increase in the d(002) spacing for the purified MWNTs with Li insertion suggests that small amounts of Li ions appear to be inserted between the graphene layers of the purified MWNTs. However, the greater increase in the d(002) spacing for the etched MWNTs confirms that more Li ions are inserted easily between the graphene layers in the etched MWNTs due to the increase in lateral defects and opened ends formed by the chemical etching.

In the first discharge derivative curves shown in Fig. 7, the peak at 0.8 V for the purified MWNTs shifted to 0.9 V for the etched MWNTs with increasing the etching time, indicating that Li ions were inserted into the inner core of the etched MWNTs through the opened ends. However, the extraction of Li ions from the inner core had a great hindrance due to the strong tendency of MWNTs for accumulation of Li ions [22]. It is believed that the insertion and extraction of Li ions into/from the inner core of the etched MWNTs were facilitated more than that of the purified MWNTs due to the shortened length of the etched MWNTs, and also the insertion of Li ions into the inner core enhanced the \( C_{\text{rev}} \) in the etched MWNTs.

The exact mechanism for the enhanced \( C_{\text{rev}} \) in the etched MWNTs compared with that in the purified MWNTs is 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 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 [15–17]. The \( C_{\text{rev}} \) in thermally [23,34,35] and chemically [32,33] oxidized carbonaceous materials is enhanced by filling of Li ions onto the lateral defects, such as micro-cavities or nanovoids formed on the surface, doping of those at the edges of graphene layers, and reaction of those with the surface functional groups containing hydrogen and oxygen. The edges of graphene layers for the etched MWNTs were increased by the formation of lateral defects on surface and opened ends. Also, the surface functional groups containing hydrogen and oxygen were formed on the surface of the etched MWNTs. Therefore, these factors of the etched MWNTs facilitated the insertion of Li ions into the etched MWNTs and enhanced \( C_{\text{rev}} \) in the etched MWNTs. The reduction of \( C_{\text{rev}} \) in the etched MWNTs for the further etching time was attributed to the increase of the disordered/amorphous carbon at the expense of the etched MWNTs.

It is evident from a large voltage hysteresis in the charge/discharge curve shown in Fig. 5 that most of Li ions were inserted below 0.25 V in the discharge process, while those were extracted almost uniformly between 0 and 3 V. This means that the extraction of Li ions from the purified MWNTs and the etched MWNTs had a great hindrance. Such a large voltage hysteresis was previously observed for MWNTs [18–23] and SWNTs [24–28], also observed for ball-milled sugar carbons [36] and soft carbons containing substantial hydrogen [37]. It is generally attributed to bonding changes in the host, or activated process such as the formation of C–H–Li [37,38] or C–O–Li [39] species [19,21,25]. Since the contents of hydrogen and oxygen consisting of the surface functional groups increased with increase in the etching time, as shown in Table 1, the large voltage hysteresis was observed in the etched MWNTs.

4. Conclusions

MWNTs were synthesized on the supported catalysts by thermal CVD and effectively purified by an acidic treatment followed by the gas-phase oxidation process. The purified MWNTs were chemically etched in an acid solution for modifying the structural characteristics and the surface functional groups of the purified MWNTs.
The $C_{\text{rev}}$ of the etched MWNTs increased with increase in the etching time from 351 mAh/g ($\text{Li}_{0.9}\text{C}_6$) for the purified MWNTs to 681 mAh/g ($\text{Li}_{1.8}\text{C}_6$). In the etched MWNTs, lateral defects, opened ends, edges of graphene layers, and surface functional groups containing hydrogen and oxygen were formed on surface of the etched MWNTs with reduction in length of the etched MWNTs. These structural and chemical modifications in the etched MWNTs facilitated the insertion of Li ions into the etched MWNTs, and hence enhanced $C_{\text{rev}}$. However, the extraction of Li ions from the etched MWNTs had a great hindrance. The $C_{\text{irr}}$ of the etched MWNTs also increased with increase in the etching time from 1012 mAh/g ($\text{Li}_{2.7}\text{C}_6$) for the purified MWNTs to 1229 mAh/g ($\text{Li}_{3.3}\text{C}_6$), due presumably to the formation of the SEI on large surface area by the chemical etching.

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References