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Electrochemical Behaviors of Functionalized Carbon Nanotubes in $LiPF_6$/EC+DMC Electrolyte

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The effect of oxidation on the surface functional groups of carbon nanotubes (CNT) through acidic agents (nitric acid and a mixture of sulfuric and nitric acid) was studied. The correlation between the amount of surface functional groups and the electrochemical properties of CNT in $LiPF_6$/EC+DMC Electrolyte was then investigated. Transmission electron microscopy (TEM) and Fourier transform infrared spectrophotometer (FTIR) suggested that oxygen-containing surface groups were successfully introduced and the highly tangled long ropes of CNT were cut into short, open-ended pipes during the acid treatment. The amount of functional groups was evaluated by acid-base titration. Charged and discharged testing and cyclic voltammetry (CV) were used to characterize the electrochemical behaviors of the samples. It is found that the electrochemical properties of functionalized CNT are primarily dependent on the amount of carboxyl groups. The sample treated with mixed acid at 70℃, which has the highest amount of carboxyl groups, exhibits both high capacity and good rate capability. The additional capacity contributed by the reversible faradic reaction from the surface groups on CNT make it possible to be assembled as a promising material in combining the distinguished properties of batteries and capacitors.

Keywords: Carbon nanotubes, Functionalization, $LiPF_6$/EC+DMC Electrolyte, Electrochemical properties

1. INTRODUCTION

Recently, Li-ion batteries and electrochemical capacitors have attracted worldwide researching interest because of their potential applications as energy storage devices in various fields. However, each of them has its own advantages and disadvantages. Li-ion batteries benefit from the highest energy density (150-200 Wh/kg), but suffer low power capability (~1 kW/kg) and limited cycle life. On the other hand, electrochemical capacitors have extremely high power capability (~10 kW/kg), unlimited cycle life, but modest energy density (2-6 Wh/kg) [1]. In order to bridge the performance gap between batteries and capacitors, one approach is to improve existing technologies, such as increasing the power capability of Li-ion batteries by employing nano-structured lithium storage materials [2-4] or increasing the energy density of electrochemical capacitors through tailoring the pore size of the porous carbon [5-7]; the other approach is to invent new hybrid energy storage systems [8, 9].

In the present study, the object is focused on the power improvement of carbon nanotubes (CNT)-based electrode in Li-ion battery systems. CNT are typical one-dimensional carbon materials with excellent electronic, mechanical and chemical properties, which are good candidates for electrode materials of both Li-ion batteries and electrochemical capacitors [10-14]. It has been know that when used in electrochemical capacitor, the specific capacitance of CNT is low due to their poor hydrophility. Considerable research efforts have been focused on improving the hydrophility of CNT by a variety of chemical treatments to produce surface functional groups [15, 16]. However, functionalized CNT-based capacitor electrodes still have a low energy density due to the low working voltage (lower than 2.7V in non-aqueous organic electrolytes) in capacitor and the almost saturated double layer capacitance per specific surface.

An alternative choice is to use the functionalized CNT electrodes in Li-ion batteries, electrolytes of which often have a high potential window (higher than 4.5V). The electrodes accumulate charge through faradaic electrochemical process (redox reaction between the surface functional groups and the electrolyte), which can not only increase the specific capacity, but also extends the working voltage. As a result, the energy density of the electrodes can be enlarged considerably, while high power capability is also provided. In this paper, we show that functionalized CNT can provide satisfactory performance as electrode materials, combining the advantages of batteries and capacitors. The influence of different kinds of surface functional groups on the electrochemical behavior of CNT electrodes is also addressed.

2. EXPERIMENT PART

2.1 Preparation and characterization

The CNT used in this work were multi-walled CNT purchased from ACS Material, with purity of 98%, outer diameter of 10-20 nm and length of 10-30μm. 500mg of pristine CNT were added into 150ml of nitric acid (68% HNO_3) and reflux at 70℃ for 4h to prepare the nitric acid oxidized sample denoted as CNT-N-70. Another two of 500mg of pristine CNT were added into 150mL of mixed acid, which were composed of concentrated sulfuric acid (98%H_2SO_4) and nitric acid (68%HNO_3) with the volume ratio of 3:1, and refluxed at 50℃and 70℃ for 4h to prepare the mixed acid oxidized samples denoted as CNT-M-50 and CNT-M-70，respectively. Then each of the mixture was diluted by large amount of de-ionized water and filtrated, washed with de-ionized water until the filtrate reached a pH of 7, and dried at 120℃ for 24h. The particle morphology and porous structure of the samples were examined by transmission electron microscopy (TEM, Tecnai G200). Infrared spectra were recorded on a Fourier transform spectrophotometer (FTIR, Perkin-Elmer 1710) using KBr pellets. The amount of functional groups was characterized by acid-base titration described in detail elsewhere [17].

2.2 Electrochemical measurements

The samples were mixed with polyvinylidene fluoride (PVDF, 9:1 mass ratio) in N-methylpyrrolidone (NMP). The slurry thus obtained was coated onto aluminum foil and dried at 120℃ in vacuum to obtain CNT electrodes. Electrochemical properties were examined in 2025 coin-type half-cell using 1 M $LiPF_6$ solution in a mixed solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) as electrolyte. The cell was built with CNT electrode as working electrode and metallic lithium as counter electrode in an Ar filled glove box in which H_2O concentration was kept below 1 ppm. The cells were charged and discharged at different rates ranging from 0.1A/g to 10A/g between 1.5 and 4.5 V versus Li/Li^+ on LAND CT-2001A (Wuhan Jinnuo Electron Co. Ltd.). Cyclic voltammetry (CV) were carried out on electrochemical analyzers PAR 2273A (PerkinElmer Inc.)

3. RESULTS AND DISCUSSION

3.1 Physical characteristics of functionalized CNT

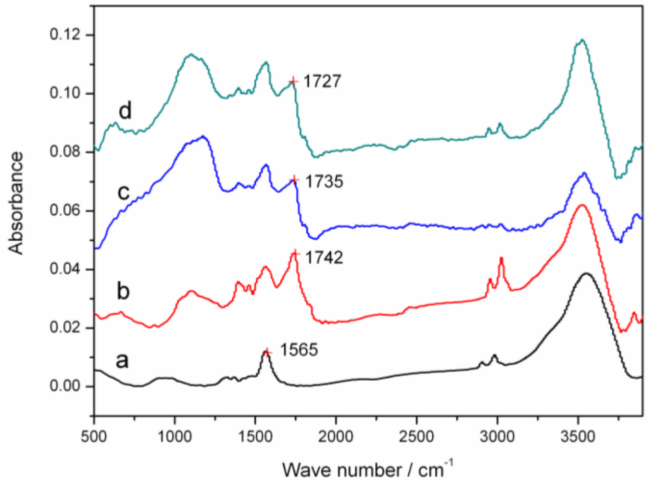

Figure 1. FTIR spectra of CNT (a), CNT-N-70 (b), CNT-M-50 (c), CNT-M-70(d)

For the sake of obtaining functionalized CNT, method of chemical modification was used. The oxidants included in this study are HNO_3 and mixed acid (at different temperature). These treatments are all effective in functionalizing the CNT but are different in oxidation ability. The type and the amount of the functional groups on the surface of CNT also vary.

Chemical modification of CNT using acid treatment has been widely studied by using FTIR [18, 19]. FTIR spectra of the as-received CNT and different acid treated CNT are given in Figure 1. The typical FTIR spectrum of the as-received CNT shows a strong infrared absorption at 1565 cm^{-1} which has been generally assigned as an in-plane E_{1u} mode of graphite structure in the literature [20]. In all the FTIR spectrums of CNT treated with acid, a new peak around 1735 cm^{-1} can be found. It is normally assigned to the C=O strength vibration in the COOH group[21], which means that all the acid treatment will introduce some COOH groups to the end of the wall of CNT. However, this new peak shifted from 1742 cm^{-1} to 1727 cm^{-1} as the HNO_3 treatment is changed to mixed acid treatment, and shifted from 1735 cm^{-1} to 1727 cm^{-1} as the temperature increase, suggesting that the formation of hydrogen bonds between the COOH groups became more effective when the oxidation ability of reagent is improved or temperature is increased.

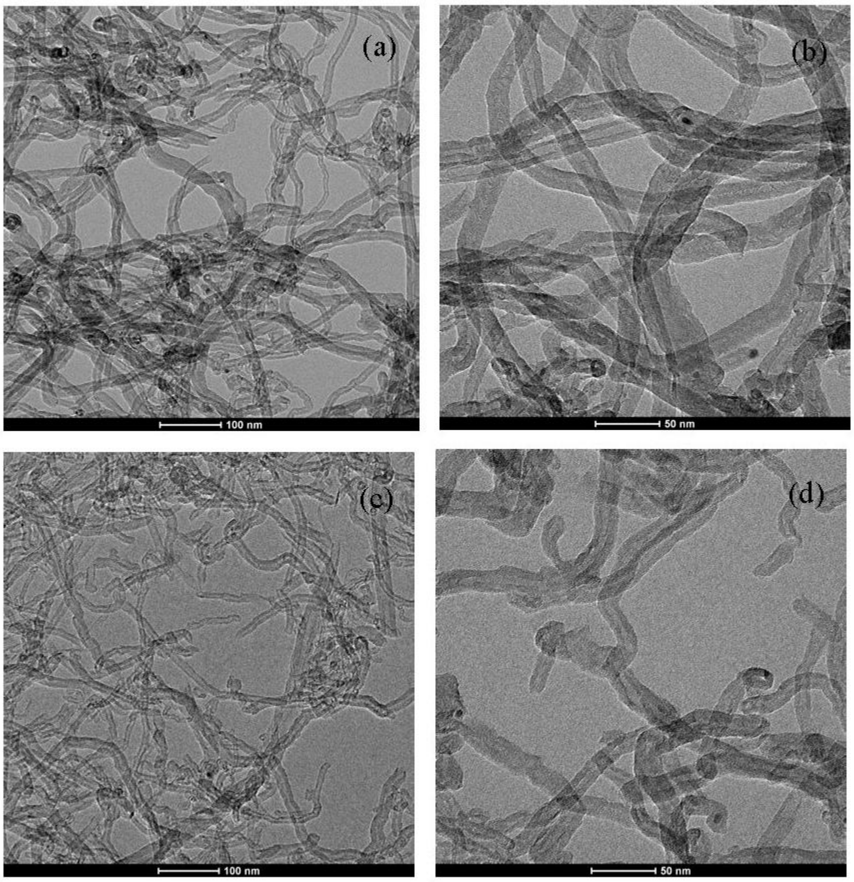

Figure 2. TEM images of CNT (a, b) and CNT-M-50 (c, d)

HNO_3 is a relatively mild oxidant and cannot generate abundant functional groups on the surface of CNT. In the case of using H_2SO_4/HNO_3 as a moderate oxidant, the mixed acid is strong enough to break the tube and generate abundance of functional groups, especially at higher temperature.

TEM images of CNT and CNT-M-50 are shown in Figure 2, which exhibits some direct visualization of the length, diameter distribution and the defects of CNT before and after treatment. In our observation, the CNT tend to exist as bundles with a typical outer diameter of 20nm and smooth surfaces, while more individual CNT appear after treated with H_2SO_4/HNO_3, indicating the use of mixed acid is an effective way to cut the highly tangled long ropes of CNT into short, open-ended pipes. Moreover, high-resolution TEM images showed very rough surfaces of CNT-M-50 (Figure 2d) compared with those of the untreated samples (Figure 2b), which may reveal that some new defects were generated on the tubes' surface. These defects are known to provide reactive sites to the reagent and thus binding with oxygenated species strongly [22].

In order to determine the concentration of the surface functional groups, a direct acid-base titration technique was performed, which using NaOH to determine the total acidic sites (including carboxylic acid, lactones and phenols) and $NaHCO_3$ to individually determine the carboxylic acid groups. In Table 1, the mmol of acidic oxygen-containing surface groups per gram of CNT material are given as a function of chemical treatment. The titration experiments demonstrate that an increase in severity of the oxidation results in an increase in the concentration of total acidic surface sites, from 2.80 mmol/g on pristine CNT to 5.03 mmol/g on nitric acid treated material (CNT-N-70), and further to 5.21 mmol/g on mixed acid treated material at the same temperature (CNT-M-70). Moreover, the mixed acid treated CNT obtained at different temperature have almost the same amount of total acidic groups but the one treated at 70℃ has higher content of carboxylic groups than that treated at 50℃ (CNT-M-50) , indicating that increasing temperature is beneficial to increase the concentration of carboxylic groups. These results are in full agreement with the FTIR data (Figure 1).

Table 1. The results of Boehm's titration

Samples	Total acid titration（mmol/g）	Carboxyl titration（mmol/g）	Ratio of carboxyl groups (%)
CNT	2.80	1.52	54.3
CNT-N-70	5.03	1.93	38.4
CNT-M-50	4.99	3.22	64.5
CNT-M-70	5.21	4.87	93.5

3.2 Electrochemical properties of functionalized CNT

Figure 3 shows the cyclic voltammogram (CV) of CNT and CNT-M-50 electrodes with different upper-and-lower-potential limits. It can be noted that the shape of CV for CNT is very close to a rectangle in both the voltage range of 1.5-4.5V and 3-4.5V, suggesting that the capacitance of

CNT is mainly contributed by electric double-layer capacitance. However, strong electrochemical polarization occurs in the voltage range of 1.5-3V while the CV still keep a rectangular shape in the range of 3-4.5V for CNT-M-50. Recent studies have shown that carboxyl groups can be reduced by lithium ions and reversibly oxidized in the voltage range from ~3.0 to ~1.5V versus Li [23]. Since the intercalating of lithium ions into the carbon layers would not happen above 1.5V [24], it can be deduced that the redox peak in the range of 1.5-4.5V is caused by a steric hindrance for Faradic reaction from the surface groups on CNT-M-50. This Faradic reaction can provide additional capacities when compared to CNT.

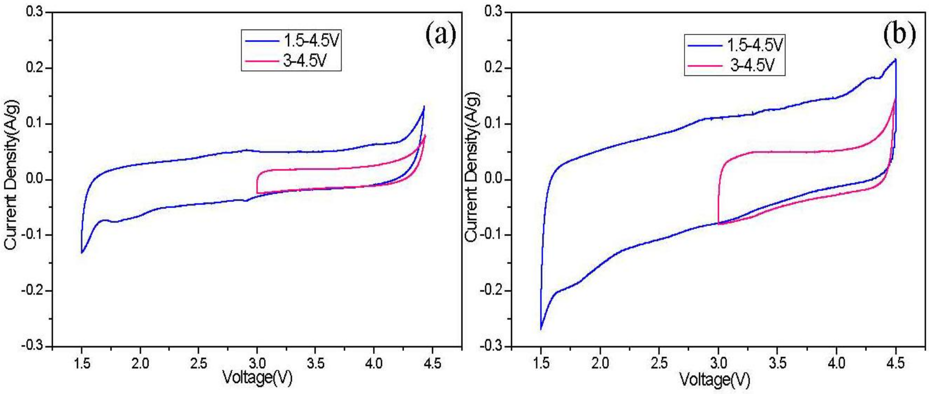

Figure 3. Cyclic voltammogram curves for pristine CNT (a) and CNT-M-50 (b) electrodes obtained with different upper- and lower-potential limits

The typical charge and discharge curves of CNT, CNT-N-70, CNT-M-50 and CNT-M-70 are presented in Figure 4.

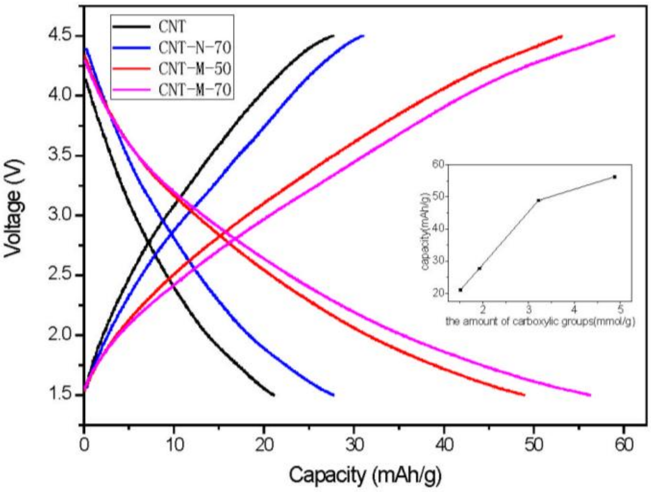

Figure 4. Charge and discharge curves of CNT, CNT-N-70, CNT-M-50, CNT-M-70 at a 0.1A/g current, inset is the relationship between the capacities and the amount of carboxylic groups

The specific capacities of four samples are 21.1, 27.7, 48.9 and 56.2 mAh/g for CNT, CNT-N-70, CNT-M-50 and CNT-M-70, respectively. On the basis of similar pore structure of the samples, it can be deduced that the increasing capacities of the functionalized samples can be attributed to the Faradic reactions of surface groups. The contribution of Faradic reactions capacity to the whole capacity become larger compared to the double-layer capacity when the total acidic surface groups increase as Table 1 listed. Furthermore, it is also worth noting that CNT-M-50 and CNT-M-70 have almost the same amount of surface groups, but the capacity of CNT-M-70 is larger than that of CNT-M-50. It can be found, by comparing the kinds of surface groups of the two samples, that CNT-M-70 has a larger amount of carboxyl groups, suggesting that carboxyl group is more effective in increasing the capacities of CNT. Figure 4 inset reflects the proportional relationship of the capacities and the amount of carboxyl groups. This result is in agreement with Ref.23 for that oxidation-reduction reaction can take place between lithium ions and carboxyl groups reversibly. The functional electrodes could store energy on both the double-layer and the surfaces of CNT, which enables them to have a high rate capability and a relatively high capacity simultaneously. Rate capability studies were done on pristine CNT and the functional samples to ascertain the performance of the materials under varying load conditions. Figure 5 gives the discharge capacity of different CNTs at various applied load conditions. The figure shows that all the functional samples maintain good rate capacity similar to that of CNT. The initial capacity of CNT-M-70 was found to be approximately 60 mAh/g at low rate of 0.1 A/g, following by somewhat capacity fading during the next several cycles. Half of the initial capacity (about 30 mAh/g) was retained at considerably high rate of 10 A/g. However, although the functional samples all gave consistently higher capacity at all rates compared to pristine CNT, pristine CNT still exhibited better rate performance than the functional ones, the rate performance of which became even worse when the capacity derived from Faradic reactions increases. This indicates that surface redox reaction is the limited process during the charge-discharge of the functional CNTs.

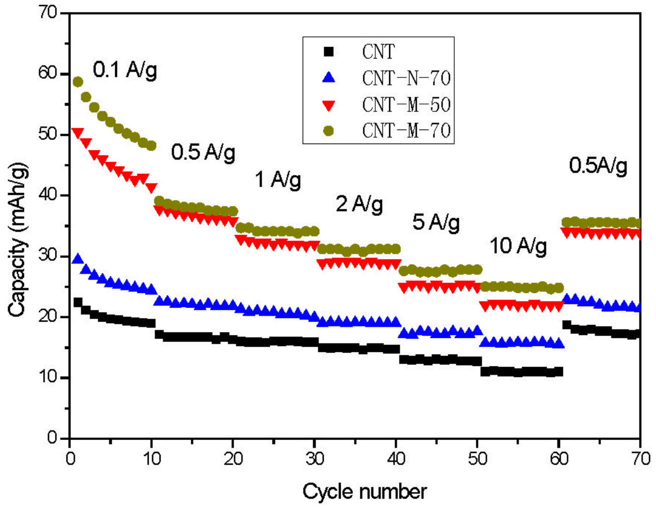

Figure 5. Rate capacity studies of CNT, CNT-N-70, CNT-M-50, CNT-M-70

The gravimetric energy and power densities of the CNT electrodes are shown in Figure 6. The functional CNT electrodes deliver much higher gravimetric energy at all powers (from ~200 W/$kg_{electrode}$ to more than 10 kW/ $kg_{electrode}$). Among the functional CNT electrodes, CNT-M-70 which has the largest amount of carboxyl groups deliver the highest gravimetric energy of about 70 Wh/$kg_{electrode}$ at a power of 10 kW/ $kg_{electrode}$. This value is much higher than that of current electrochemical capacitors based on CNT electrodes.

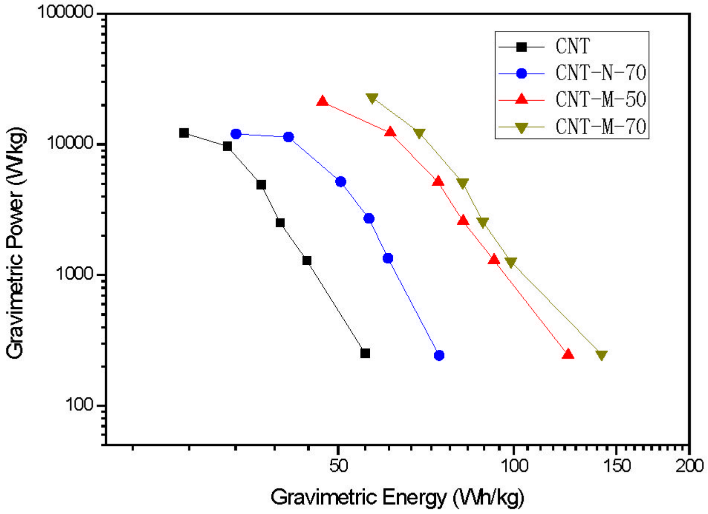

Figure 6. Ragone plot for CNT, CNT-N-70, CNT-M-50, CNT-M-70

4. CONCLUSIONS

The relationship between the amount of surface functionalized groups and electrochemical properties of CNT is investigated with different oxidation treatments for the sake of controlling the content and composition of surface functionalized groups. Comparing to nitric acid treatment, it is found that mixed acid treatment is an effective way in preparing a promising material used in power batteries which can deliver large gravimetric energy at very high power. In addition, the proportion of carboxyl groups, which contribute to the capacitance of CNT electrode mainly via Faradic reactions, is dependent on treating temperature. The CNT treated by the mixed acid at 70℃ has the highest initial capacity and gravimetric energy as a result of the largest amount of carboxyl groups.

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