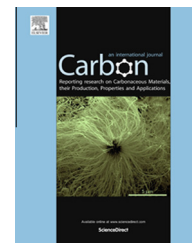


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# Cycle and rate performance of chemically modified super-aligned carbon nanotube electrodes for lithium ion batteries



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## ABSTRACT

Super-aligned multi-walled carbon nanotubes (MWCNTs), which had been produced in large-scale, were oxidized by  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ . The surface defects and oxygen-containing functional groups introduced during the oxidizing process were characterized by Raman spectroscopy and X-ray photoelectron spectroscopy. The surface modification of MWCNTs improved the electrochemical properties. As a result,  $\text{H}_2\text{O}_2$ -treated and  $\text{HNO}_3$ -treated MWCNTs displayed reversible capacities of 364 mA h/g and 391 mA h/g, respectively, after 80 galvanostatic cycles, corresponding to 143% and 154% improvements compared with pristine MWCNTs. The rate capability was also increased. At a current density of 3500 mA/g,  $\text{H}_2\text{O}_2$ -treated and  $\text{HNO}_3$ -treated MWCNTs exhibited reversible capacities of 66 mA h/g and 156 mA h/g, respectively. In contrast, pristine MWCNTs were only able to deliver 27 mA h/g at this current density.

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## 1. Introduction

Carbon nanotubes (CNTs) have long been considered as a promising candidate for electrode materials in lithium ion batteries (LIBs) [1–4]. Comparing with commercialized graphite anode, the tubular, defect-free, and integral structure of pristine CNTs suggests a different mechanism of  $\text{Li}^+$  insertion/extraction in contrast to intercalation process to the graphite structure. Experimental work found that pristine single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) showed reversible capacities of only 300 mA h/g [5] and 273 mA h/g [6] after 5 cycles, both were lower than the theoretical capacity of graphite (372 mA h/g in terms of  $\text{LiC}_6$ ). To explain these low capacities, theoretical simulations revealed that the diffusion of  $\text{Li}^+$  through the sidewalls of CNTs experienced large energy barriers [7–9]. An ab-initio investigation suggested that such diffusion energy barriers would decrease from 13.5 to 0.5 eV, when

topological defects on CNTs were introduced [7]. Therefore, the lithium storage of CNTs is related to a defect-dependent mechanism and the introduction of lateral defects on the CNT sidewalls was identified as an effective strategy to improve the capacity. In this regard, approaches such as chemical etching or mechanical ball milling were explored. For instance, electrochemical measurements of chemically etched and mechanically ball-milled CNTs showed enhanced reversible Li capacities of 681 mA h/g ( $\text{Li}_{1.8}\text{C}_6$ ) [10] and 641 mA h/g ( $\text{Li}_{1.7}\text{C}_6$ ) [11]. However, these results were still deficient in terms of long-term cycle stabilities, as only several initial cycles were included. More importantly, further discussions on the long-term performance at a variety of high rate tests were little emphasized.

Another issue in up to date publications involving the electrochemical characterization of CNTs lies in their intrinsic properties. Indeed, the electrochemical performance of CNT is dependent on the morphological factors such as aspect

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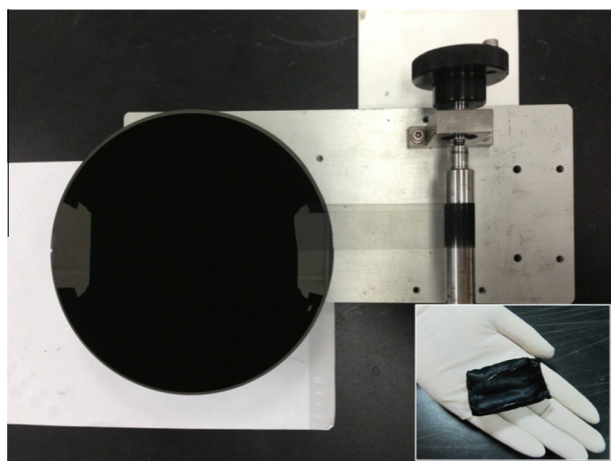
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ratio, curvature, and quality of crystallization. Moreover, the scattered quality of each CNT batch will hardly lead to an unambiguous conclusion. To improve this, we choose super-aligned MWCNTs synthesized in a low-pressure chemical vapor deposition (CVD) system [12–14]. Since the yield and quality of such MWCNTs have met industry-level requirements and the property is quite uniform, stable characterizations of long-term cycle and rate performance could be expected. Another significance is that self-sustained MWCNT films could be directly drawn from super-aligned MWCNT arrays. This mechanical property will guarantee freestanding electrodes in escape of organic binders and conductive additives. Nor metal current collectors are required. Thus, the mass of electrode could be precisely measured and side effects would be minimized. The MWCNT electrodes will be chemically oxidized by two reagents,  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$ , and characterized by transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). In order to better understand the interactions between lithium and MWCNTs, the cycling stabilities of differently treated samples are systematically discussed on the basis of galvanostatic charge and discharge cycles, cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). Finally, the rate performance is also evaluated by applying a series of high current densities to MWCNT electrodes.

## 2. Experiment

Super-aligned MWCNT arrays on 4-inch silicon wafers with a diameter of 20–30 nm and a height of 300  $\mu\text{m}$  were synthesized in CVD with iron as the catalyst and acetylene as the precursor. The synthesis procedure could be viewed in previous studies [12–14]. The MWCNT film could be drawn from the MWCNT arrays, following an end-to-end joining mechanism, and collected on a stainless steel roller (see in Fig. 1). A razor blade was used to cut off the MWCNT film (inset of Fig. 1).



**Fig. 1 – Preparation of MWCNT film from MWCNT arrays on a 4-inch silicon wafer with a metallic roller. Inset: photograph of pristine MWCNT sample just cut off from the roller. (A colour version of this figure can be viewed online.)**

Chemical modification of MWCNTs was carried out in two different kinds of oxidants, 30 wt.%  $\text{H}_2\text{O}_2$  and 70 wt.%  $\text{HNO}_3$ , respectively. For  $\text{H}_2\text{O}_2$ -treated sample, an as-prepared 20 mg MWCNT film was immersed in 50 mL  $\text{H}_2\text{O}_2$  in a 100 mL round bottom flask. The reaction was then refluxed at 100 °C for 8 h. The resulted MWCNT dispersion was vacuum filtered and washed with distilled water until neutral pH. The sample was finally dried at 80 °C overnight. The  $\text{HNO}_3$ -treated sample was prepared in a similar condition but only refluxed for 2 h. The sample was also washed with distilled water, and dried at 80 °C overnight. Both treatments would result in freestanding CNT films with yields over 80%.

The morphology and microstructure of chemically modified CNT were studied in a FEI Tecnai G2F20 transmission electron microscope operating at 200 kV. Raman spectra were recorded on a Horiba spectrometer (514 nm Ar laser, 24 mW). XPS analysis was carried out on a Thermal Escalab 250xi spectrometer (50 kV, Al target). C1s XPS spectra were deconvoluted into Gaussian–Lorentzian type peaks after applying a Shirley background.

All electrochemical characterizations were performed in CR2016 coin-type cells that were assembled in an argon-filled glove box (M. Braun Inert Gas Systems Co. Ltd.). Lithium foil was used as the counter electrode for all measurements. A porous polymer film (Celgard 2400, USA) was used as a separator. There was no Cu foil as a current collector in this cell assembly. The electrolyte was 1 M  $\text{LiPF}_6$  in a mixture of ethylene carbonate and diethyl carbonate with a volumetric ratio of 1:1. The galvanostatic discharge–charge process was measured on a Land battery testing system (Wuhan Land Electronic Co., China) from 0.01 to 3 V. Different specific currents densities ranging from 35 to 3500 mA/g were applied for the different rate characterization. CV experiments were performed on a potentiostat/galvanostat electrochemical system (PARStat 2273) in the voltage range of 0.01 to 3 V with a scan rate of 0.1 mV/s. EIS results were collected on the same apparatus with a perturbation input of 10 mV over the frequency range from 100 kHz to 100 mHz. After electrochemical tests, MWCNT electrodes were taken out and washed with ethanol and distilled water for post-cycle characterizations.

## 3. Results and discussion

### 3.1. Morphological analysis

The as-grown MWCNT array can be easily drawn into a thin MWCNT film that only consists of single-layered MWCNT yarns arranged in a parallel fashion. The thin MWCNT film was rolled onto a stainless steel cylinder to make freestanding MWCNT electrodes, as shown in Fig. 1. The junction in MWCNTs can be attributed to van der Waals interactions [12]. For oxidized samples, the shape of MWCNT films can be restored after the vacuum filtration process. Fig. 2 showed TEM analysis of the morphology of pristine and chemically modified MWCNTs. The graphitic lattice of pristine MWCNTs can be clearly observed. However, the sidewall was covered with a layer of rough deposit, which was probably a result of hydrocarbon residue during the CVD (see in Fig. 2a). The overall morphology of the chemically modified MWCNTs

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