



Deeply fluorinated multi-wall carbon nanotubes for high energy and power densities lithium/carbon fluorides battery



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ABSTRACT

Deeply fluorinated multi-wall carbon nanotubes (F-MWCNTs) with different diameters are prepared using the mixture of fluorine/nitrogen gas, and the molar ratio of fluorine to carbon is controlled to be approximate to 1. The electrochemical performances of F-MWCNTs are tested as the cathode material in primary lithium battery. The discharge rate of 4 C can be applied for these F-MWCNTs and F-MWCNTs with average diameter larger than 50 nm can support the high discharge rate up to 5C delivering a maximum power density of 7114.1 W kg⁻¹, associated with a high 1923 Wh kg⁻¹ energy density. The conductive networks of intimately contacting MWCNTs in nano-scale and the intrinsic fast rate capability of one-dimensional nanostructures account for the high power density of F-MWCNTs. Moreover, F-MWCNTs with larger diameter exhibits better electrochemical performances. Based on the pore size distribution and impedance results, it is proposed that the F-MWCNTs with larger diameters can effectively avoid the surface and networks of F-MWCNTs being blocked by the enlarged LiF crystals, and hence display the better electrochemical performances.

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1. Introduction

The lithium/carbon monofluoride (Li/CF_x) was one of the first lithium/solid cathode systems to be commercialized [1–3]. The theoretical specific energy of this system is 2180 Wh kg⁻¹ and is the highest value among the solid cathode systems. Due to the relatively high cost of CF_x compared to other solid cathodes like manganese dioxide, it is restricted to specialized applications such as biomedical and military, where its superior characteristics are required. CF_x is highly resistive and requires a supporting conductive matrix to enhance charge transfer, which leads to initial potential delay and low rate capability, inhibiting it to be used in high-power devices. To solve this problem, sub-fluorinated carbon materials were proposed as the alternative candidates [4]. For example, sub-fluorinated carbon nanofibres could sustain high discharge rate up to 6 C thanks to the presence of unfluorinated path within the CF_x [5]. The preparation of CF_x at low temperature with the help of Lewis Acids was another approach to improve the electronic conductivity of CF_x through the formation of ionic or semi-ionic C–F bond rather than covalent C–F bond [6,7]. However, the relative low fluorine content limited the capacity and the residual Lewis Acids usually initiated the self-discharge of

Li/CF_x battery [8]. The mixture of CF_x with other cathode materials such as manganese dioxide or silver vanadium oxide to develop a hybrid structure was also applied to modify the rate capability of Li/CF_x battery [9,10], but the progress in this area was limited without significant improvement on the rate performance. Recent investigations have been focus on improving the electrochemical performances of Li/CF_x battery by coating the surface of CF_x with conductive layers [11,12] or adding highly conductive additives to the paste [13,14].

One-dimensional (1D) nanostructures provide a direct pathway for efficient charge transport along its micro-scale axis, while the two radically small nano-scale dimensions drastically reduce the ion diffusion length. Owing to the unique merits, 1D nanostructures have fast rate capabilities and have been intensively studied for application in electrochemical energy storage devices [15–18]. Carbon nanotubes (CNTs) possess unique structure and electronic properties, such as a good conductivity and a high surface area to weight ratio as well as the ability to form a three-dimensional conducting network. The potential use of fluorinated carbon nanotubes (F-CNTs) as a high energy density cathode material of Li/CF_x battery is expected, particularly for the deeply fluorinated ones. It has been demonstrated that F-CNTs exhibited a stable operation potential [19,20] and a faradic yield [21] at low discharge rate. However, the rate capability of F-CNTs has not been investigated yet, especially these with deep fluorination.

The purpose of this study is to investigate the discharge performances of deeply fluorinated multiwall carbon nanotubes

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(F-MWCNTs) with different diameters. The molar ratio of fluorine to carbon (represented as F/C) of F-MWCNTs was controlled to be close to 1, insuring the deep fluorination. The synthesized F-CNTs exhibited excellent rate capability without loss of the specific capacity at low rate due to the deep fluorination. In addition, it was initially found that F-MWCNTs with larger diameter showed better discharge performances and the corresponding mechanism were discussed in this study.

2. Experimental

2.1. Preparation of F-MWCNTs

Multiwalled carbon nanotubes (MWCNTs) with different diameters, which were labeled as MWCNT1 (diameter ≤ 8 nm), MWCNT2 (diameter in the range from 20 to 30 nm) and MWCNT3 (diameter ≥ 50 nm), were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Science. They were synthesized by the catalytic pyrolysis of natural gas using Ni as the catalyst at high temperature (purity $> 95\%$). Raw MWCNT were purified by nitric acid at 90°C for 1 h to remove the residual metal catalysts and the amorphous carbon. The fluorination of MWCNT was carried out under the mixed gas stream of F_2/N_2 (1:3, vol.) in a nickel reactor. In the typical experiment, 200 mg MWCNT1, MWCNT2 and MWCNT3 were fluorinated at 380°C , 420°C and 450°C , respectively, for 24 h so as to insure the deep fluorination.

2.2. Characterizations of F-MWCNTs

Fourier transform infrared (FTIR) spectrometer was measured by infrared spectrophotometer JASCO Corporation FT/IR-300E. X-ray photoelectron spectroscopy (XPS) analyses were performed on PHI 1600 model surface analysis system with a 450 W Mg $\text{K}\alpha$ X-ray (1250 eV) source at a base pressure within the range of 10^{-8} to 10^{-9} Torr. The morphology was observed by Philips Tecnai G2 F20 field-emission transmission electron microscopy (TEM). The surface characteristics of different F-MWCNT were determined by the gas desorption and an automated gas absorption apparatus (Quantachrome NOVA-2000, N20-14D) was employed. The true density of F-MWCNT was measured by Quantachrome helium Ultrapycnometer 1000, and it was calculated as the average value of three individual measurements.

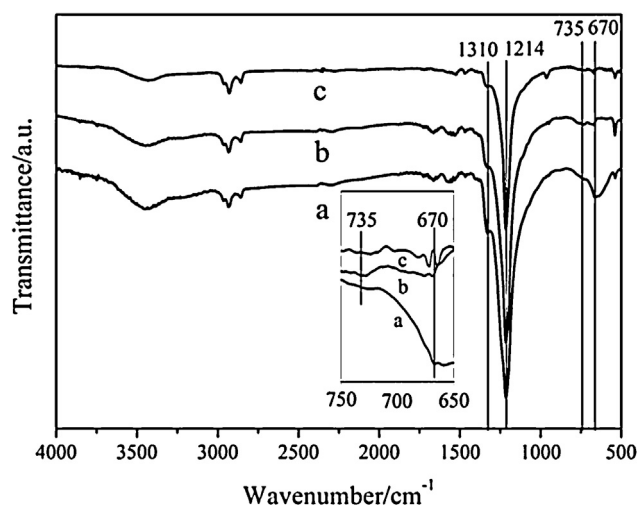


Fig. 1. The FTIR spectra of F-MWCNT1 (a), F-MWCNT2 (b) and F-MWCNT3 (c). Inset: the FTIR spectra from 650 to 750 cm^{-1} .

Table 1

Composition contents and the calculated F/C values from XPS data of F-MWCNT.

Sample	Composition from XPS (at%)			
	C	O	F	F/C
F-MWCNT1	48.5	2.4	49.1	1.012
F-MWCNT2	48.3	3.2	48.5	1.004
F-MWCNT3	49.0	2.8	48.2	0.983

2.3. Electrode preparation and electrochemical measurements

The electrodes were composed of F-MWCNTs (75 wt%), Super P carbon (15 wt%) as the conductive additive and polyvinylidene

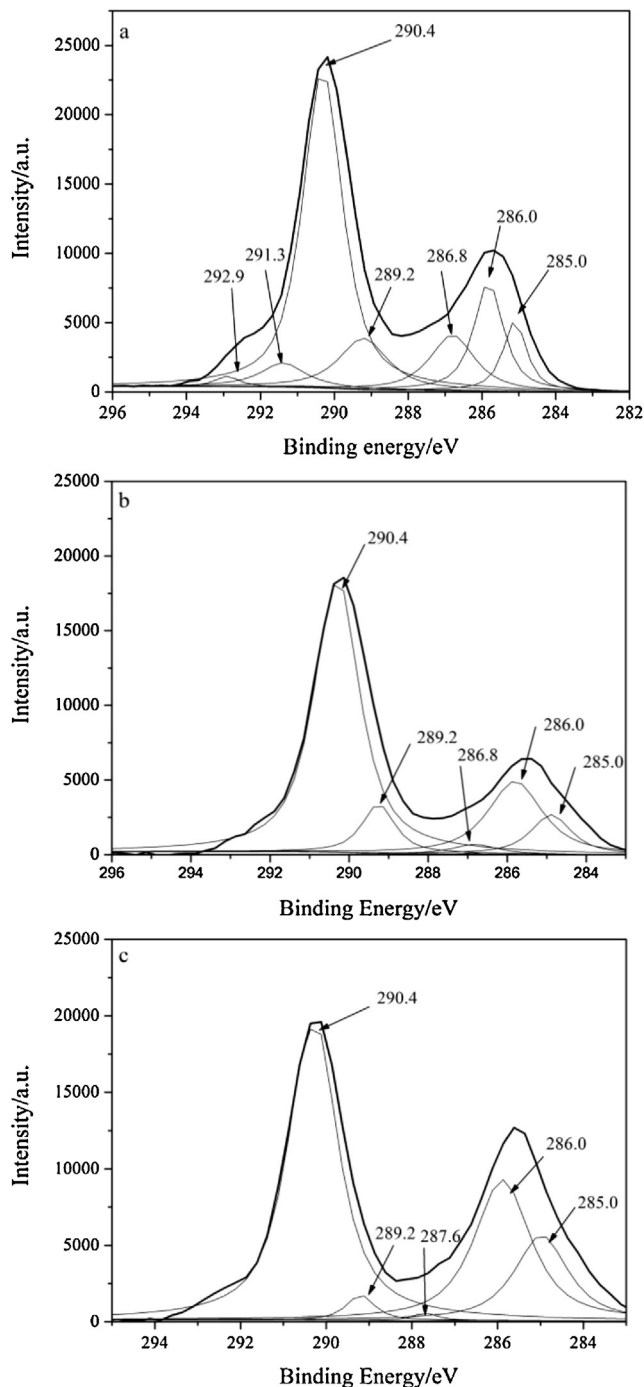


Fig. 2. The C1s spectra of F-MWCNT1 (a), F-MWCNT2 (b) and F-MWCNT3 (c).

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