Journal of Physics and Chemistry of Solids 75 (2014) 60–67

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Morphology of carbon nanostructures and their electrochemical performance for lithium ion battery

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ARTICLE INFO

Article history:
Received 12 July 2013
Received in revised form
19 August 2013
Accepted 24 August 2013
Available online 30 August 2013

Keywords:
A. Nanostructures
B. Vapour deposition
C. Electron microscopy
C. Raman spectroscopy
D. Electrochemical properties.

ABSTRACT

A comparative study has been carried out on anodes made from carbon nanostructures of five different morphologies—single walled, double walled and multiwalled carbon nanotubes (with two different diameters), and carbon nanofibers. The specific area of the samples of these carbon nanostructures has been determined and their structure and morphology have been characterized by microscopy, X-ray diffraction and Raman spectroscopy. Depending on the morphology and the size of the nanostructures in the anode, the reversible capacity obtained ranges from 450 to 600 mAh g^{-1} and the coulombic efficiency is in the range of 85–98% after 12 cycles. Increasing the surface area, both inside and outside for the tubes of a nano-size, gives rise to increased number of surface sites, which may be intercalated reversibly leading to increased specific charge capacity. Formation of the solid electrolyte interface layer covers a part of these surface sites as well as results in capacity fading, which also increases with increasing surface area. Increased defect sites responsible for elastic scattering in Raman spectra do not appear to have deciding influence on either enhanced capacity or capacity fading. Nano-sized constituent in the electrode appears to improve mechanical characteristics ensuring good mechanical integrity on cycling and high coulombic efficiency.

1. Introduction

Since commercial launching of lithium-ion batteries by Sony Corporation in early 1990, their uses have grown rapidly to occupy a significant market share amongst rechargeable batteries [1]. There is continuing global effort to develop lithium ion batteries with higher capacity and better stability in order to extend their applications, particularly to mobile tools and automobiles. The battery performance solely depends upon the capacity of electrode materials to hold active species of lithium and their reversible discharge/charge. The currently used commercial anode of graphite has excellent stability and low cost but could only be intercalated to a maximum of LiC_6 i.e., one lithium for six carbon atoms, leading to a theoretical limit of its specific charge capacity, 372 mAh g^{-1} [2]. With the objective to achieve higher capacity, there has been considerable effort to develop alternate anode materials for lithium ion batteries, particularly amongst metal oxides, carbonaceous materials, phosphates and sulphides. Silicon and SnO_2 have been investigated extensively because of their very high theoretical specific charge capacities of ~4200 and ~1500 mAh g^{-1}, respectively [3], but both these materials suffer from the limitation that they experience large expansion and contraction during intercalation and de-intercalation, resulting in pulverization and capacity loss. Carbon nanostructures (CNS) have been used in electrodes, with the aim to obtain higher lithiation capability and better overall performance [4]. It has been possible to charge single walled carbon nanotubes (SWCNT) up to one lithium ion for every two or three carbon atoms, which is significantly more than that of LiC_6 [5]. However, enhanced lithiation does not significantly increase the maximum reversible capacity [6,7] and so, their application in battery does not offer any advantage. Recently, higher reversible capacities have been reported in SWCNT anode, when defects are introduced in it through extra processing steps of etching or ball milling [8,9] which, however, may have implication in terms of added cost. Even though the initial specific capacity is high, the stability or the columbic efficiency has not reached the level required for commercialization. CNS have shown good stability in the long run when there is adequate degree of graphitization [10] but the specific capacity has been observed to increase with increasing creation of defects or amorphous regions [11]. In view of different claims, often contradictory, the present work has been undertaken to compare different morphologies of CNS like SWCNT, double walled carbon nanotube (DWCNT), multiwalled carbon nanotube (MWCNT) and carbon nanofiber (CNF)

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http://dx.doi.org/10.1016/j.jpcs.2013.08.009

in order to understand the influence of morphological features and defects on the electrochemical performance for application in the anode of lithium ion batteries.

2. Experimental

2.1. Synthesis of CNS and purification

Five different morphologies of CNS viz. SWCNT, DWCNT, MWCNT with two different diameters and CNF have been tested electrochemically and among which the MWCNT with larger diameter and CNF have been prepared by the process mentioned below. The other three types of CNS—SWCNT (TNS), DWCNT (TND) and MWCNT of smaller diameter (TNM3), were purchased from Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences, China.

To prepare the desired morphologies of CNS by the catalytic chemical vapour deposition method, nanoparticles of cobalt and nickel oxides doped with copper oxide, prepared by the aqueous sol–gel route, were loosely spread over the alumina boat without use of any substrate and the boat was then placed in a horizontal tubular furnace heated to a temperature of 600 °C and then ammonia gas was introduced at a rate of about 60 sccm at atmospheric pressure. The temperature of the furnace was increased to 640 °C and acetylene gas was introduced along with flowing ammonia gas for 5–15 min. The flow rate of acetylene gas was controlled at 20 sccm [12]. CNS prepared in our laboratory along with other forms of carbonaceous materials, as well as those purchased, were treated in a solution of 6 M of acid of HNO_3/HCl/HF or their mixture for cleaning, which was followed by washing thoroughly with double ionized water. Finally, the samples were dried in an oven at 120 °C. Then the dried samples were heated at about 400 °C in air to remove the remaining amorphous carbon present even after acid treatment and also to get better quality of CNS in terms of graphitization.

2.2. Physical characterizations

X-ray diffraction (XRD) patterns of the samples of CNS were taken using a Bruker AXS, D8 advance with CuK_α radiation (1.5418 Å). The morphology of the CNS was examined under field emission scanning electron microscope (FESEM) (FEI QUANTA 200 F). Transmission electron microscopy (TEM) of the CNS samples was carried out under JEOL-2100 HRTEM, FEI Tecnai F20-G2 FEGTEM and JEOL 200CX with an operating voltage of 200 kV. The dimensions of the CNS were measured using the 'Image J' plug-in on FESEM/TEM micrographs. A Renishaw 1000 Ramascope spectrometer and Renishaw inVia with an Argon ion type 514 nm wavelength (green visible light) excitation laser were used and several spectra were taken from different samples. Raman spectra were processed using the Renishaw WIRE 2.0 software and also, Origin 8.0 software, applying a multi-peak Gaussian fit. The Brunauer–Emmett–Teller (BET) specific surface area of the CNS was determined through a nitrogen adsorption/desorption isotherm with a Micromeritics Chemisorb 2720. Prior to the adsorption process, the samples were out gassed at 150 °C for at least 2 h.

2.3. Cell fabrication and electrochemical characterizations

Different types of CNS samples were used as active material for preparing the negative electrode of the test cell. Preparation of different types of CNS based electrode involves mixing each type of CNS (70–75 wt%) with 10–15 wt% of carbon black (MITSUBISHI™ Conductive Carbon Black; Mitsubishi Chemical Corporation, Japan), a binder material (Polyvinylidene fluoride) (15 wt%) (Symarit®PVDF; Quadrant Polypenco Japan Ltd.) and N-methyl-2-pyrrolidinone (NMP, Sigma Aldrich, 99.5%) as an organic solvent to a slurry, which was then spread homogeneously onto a copper foil of thickness ~10 μm and dried at 120 °C in vacuum oven for 12 h and then pressed between steel rollers. Teflon made electrochemical cells were assembled using the CNS based composite coated copper foil of 1 cm^2 area as the working electrode and lithium metal (Aldrich, 99.9%) as the counter electrode. The electrodes were separated by a microporous separator (Celgard 2400) saturated with electrolyte solution of 1 M $LiPF_6$ in ethylene carbonate (EC):diethylcarbonate (DEC) in 1:1 v/v ratio (Mitsubishi Chemical Corp.). The cells were assembled in an argon-filled glove box (MBRAUN: MB 200G) with less than 0.1 ppm of oxygen and water content and were charged and discharged in the potential window of 0.01–3.00 V vs. Li/Li^+, using the ARBIN electrochemical analyzer (BT-2000) at a rate of 0.1 C assuming 1 C is equivalent to 372 mA for pure graphite based electrode.

3. Results and discussion

3.1. Physical characterization of the CNS

The structural characteristics of different CNS samples in respect of size and surface area are reported in Table 1 along with XRD results on lattice parameter and full-width at half-maximum (FWHM) of (002) peak.

The phases and purity of different CNS were checked by XRD and the diffraction patterns are shown in Fig. 1. The presence of (002) graphitic reflection in the XRD pattern of SWCNT indicates the presence of turbostratic graphite, MWCNT, ordered graphite or their combination as well. The XRD pattern for DWCNT is similar to SWCNT and similar inference about the presence of other forms of carbon may be drawn. The diffraction peaks corresponding to the (002) graphitic plane are observed in MWCNT and CNF and it belongs to hexagonal phase (*P63/mmc*; 194) of graphitic carbon. The peak at ~44 degree corresponds to the (101) graphitic plane for MWCNT and CNF though it coincides with the nickel oxide particles and it may be noted that for MWCNT(L) with larger diameter prepared in the laboratory, the peak is more sharp due to the presence of more catalysts nanoparticles lying inside the CNS. The line shape of the (002) peak is related to the variation of the interlayer spacing and orientation of the tube to the X-ray incident beam [13] and the FWHM of each type of CNS is given in Table 1. Based on Bragg's equation, it is observed that between (002) planes, the interplanar spacing (d_{002}) is approximately 0.34 nm similar to that in graphite, but varies slightly in different types of CNS as given also in Table 1 and shown in Fig. 1. In graphitic carbon or MWCNT/CNF, the spacing of (002) increases slightly with increasing tube diameter as shown in Fig. 1(b).

The HRTEM image in Fig. 2(a) shows that the structural arrangement of the CNS is not purely graphitic as there are disordered regions between graphitic regions (inset). The defects due to twisted and turned structures of CNS sometimes with open ends, as shown in Fig. 2, may provide the sites for enhanced lithiation but it may not be easy to remove lithium from all these sites during delithiation. This situation results in high specific capacity during initial charging–

Table 1
Dimension and other physical characteristics of CNS as obtained from FESEM, TEM, BET and XRD.

Type of CNS	Physical properties			XRD	
	OD (nm)	L (μm)	BET ($m^2\ g^{-1}$)	FWHM (002 peak)	Lattice spacing d_{002} (Å)
SWCNT	1–2	5–30	380	2.404	–
DWCNT	2–4	50	350	3.887	3.437
MWCNT(S)	10–20	10–30	212	2.14	3.447
MWCNT(L)	100–200	1–10	165	5.513	3.479
CNF	200–600	5–50	57	1.934	3.493