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Effect of wrinkles on electrochemical performance of multiwalled carbon nanotubes as anode material for Li ion battery

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ABSTRACT

A 1-D monohybrid of multiwalled carbon nanotubes and graphene sheets, graphene wrapped multiwalled carbon nanotubes (gC) structure, synthesized in a template-free simple chemical vapor deposition technique without any chemical functionalization, was employed as efficient anode material for Li ion battery. Graphene nanosheets affixed to the multiwalled carbon nanotubes (MWNTs) surface by van der Waal's attraction gives a wrinkled surface to the final 1-D gC configuration. The protrusions on the surface of the tube enhances the porosity of the system and also acts as defects, enhancing lithium adsorption sites while the inner MWNT core gives high electrical conductivity, resulting enhanced electrochemical performance of 373 mAh g^{-1} at 100 mA g^{-1} current density after 150 cycles.

1. Introduction

The increasing demand of energy in the society asks for an urgent need of energy production as well as storage devices. Li ion batteries (LIBs) are one of the interesting electrochemical energy conversion and storage devices in this aspect. To meet the energy demand, higher performance LIBs with high and reversible capacity are desirable. Commercial graphite anode material with a stoichiometry of LiC_6 delivers a maximum capacity of ~300 mAh g^{-1} [1] with theoretical capacity of 376 mAh g^{-1}, which is 10 times lower than Li metal (3860 mAh g^{-1}). To get superior capacity of the battery with high power density, the Li/C ratio has to be increased with the easiness of Li intercalation and de-intercalation. With the discovery of graphene [2], 2-D allotrope of graphite, the probability of intercalating of Li ion is increased. Drawbacks such as presence of oxygen containing functional groups in the synthesized graphene sheets giving high irreversible capacity loss due to solid electrolyte inter-phase (SEI) formation, restacking upon charging-discharging, leads to poor rate performance of graphene as anode material. 1-D allotrope of graphite, carbon nanotubes are already known as viable 'molecular container' for lithium ion cause of their unique physical and electrical properties [3–5]. In case of single walled carbon nanotubes (SWNT), Li ions can intercalate in the interior of the tube and the space between the tubes, giving a maximum Li utilization configuration [6]. Bulk amount of the material is needed for commercialization of the anode material, which is a trouble for SWNTs. Multiwalled carbon nanotubes (MWNTs), on the other hand, are easier to synthesis in bulk amount compared to SWNTs [7], and are competent to insert Li^+. Lithium ion can interact with MWNTs in an approach analogous to graphite as they are nothing but multiple graphene nanoribbons placed at a distance of 0.34 nm, in the shape of concentric rolls. Added to this, as already known, the electronic structure of the material shows the main effect on the capacity value [8], high electrical conductivity of MWNTs provides faster electron transfer giving improved kinetics. But, the specific capacity of the carbon nanotubes based material for Li ion battery depends on many important aspects such as structure of the material (such as diameter, length, chirality), surface morphology, interaction between Li and carbon and type of defects present, alignment nature of the system etc [4,9–12]. Direct Li ion diffusion through the side walls of MWNTs to the interior is prohibited, giving loss of lithium upon cycling, but once inside the tube, they are not diffusion limited [13]. On this account, topological defects, open ended or damaged nanotubes of short length were employed to show improved lithium storage performance [4]. Chemical etching, ball-milling treatments were done to induce surface defects and shortening the length and their roles were extensively studied to show shortened length with wider walled and metallic MWNTs can perform better with aligned

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morphologies altering the capacity in a order scale of tens of mAh g^{-1} compared to the non-aligned [4,14]. Other optimizations like structural changes and chemical modifications via doping etc. have been studied for enhancement of the overall performance of carbon nanostructures as well as MWNTs to be an effective anode material [15–18]. Hybrid configuration of the 1-D and 2-D carbon nanomaterials are already reported to show higher performance than their individual counterparts [18–23]. While the effect of the structure of the material are reported extensively, role of defects are yet to be specified, which are considered to increase the performance by improving adsorption and diffusion of Li^+.

In this present work, we have employed wrinkled surfaced graphene wrapped multiwalled carbon nanotubes (gC) as the anode material to study the effect of defects in terms of fragmentations, multi-curvatures and protrusions at the surfaces of gC to compare its electrochemical performance over smooth MWNTs.

2. Experimental section

2.1. Material Synthesis

Graphene wrapped carbon nanotubes (gC) were synthesized in a customized catalyst assisted chemical vapor deposition technique as reported by us earlier [24]. Briefly, misch metal based alloy ($MmNi_3$) hydride was used as the catalyst for the growth of multiwalled carbon nanotubes (MWNTs) with acetylene precursor [7]. Graphite oxide (GO), prepared by modified Hummers' method [25] was employed as the graphene precursor. For the synthesis of gC, alloy catalyst and GO were mixed mechanically using a mortar and pestle, in a weight ratio of 1:1. The fine mixture was sprinkled over a quartz boat and positioned inside a tubular chamber with controlled atmosphere and temperature. The system was heated to 250 °C in hydrogen flow for 30 min., until further increment of temperature to 700 °C in acetylene gas flow. Argon gas was allowed to flow throughout the whole procedure. Nanotubes growth atmosphere was maintained for optimized 30 min, before switching off the furnace. The as grown sample was collected after cooling down to room temperature and air oxidized at 400 °C before removing the unused metal catalyst impurity by acid treatment (H_2SO_4: HNO_3 = 3:1). The final product was labeled as graphene wrapped carbon nanotubes (gC). This active material was used for anode slurry preparation without any further chemical modification.

2.2. Physical Characterizations

To study the morphology and uniformity of the synthesized samples, field emission scanning electron microscope (FESEM, FEI QUANTA 3D) was used. X-ray diffraction (XRD) patterns were recorded for the synthesized samples in a PANalytical X'Pert Pro X-ray diffractometer with Nickel filtered Cu-Kα radiation source (λ=0.15406 nm) at 40 kV and 30 mA, in the range of 5°–90° (2θ). The vibrational modes of the samples were studied in a WiTec Alpha 300 with 532 nm, Nd: YAG laser as excitation source. Laser intensity was adjusted so that not to burn the sample and kept fixed throughout the measurements. High-resolution transmission electron microscopy (HRTEM, Technai G20 (200 kV)) instrument was used to study the nature of wrapping on the surface and overall morphology of the synthesized samples. Holey carbon coated 200 mesh copper grid was used for this study with the samples ultrasonicated in ethanol and drop casted on it. Brunauer–Emmett–Teller (B–E–T) surface area analysis was done by nitrogen adsorption–desorption isotherms at liquid nitrogen temperature of 77 K using a Micromeritics ASAP 2020 instrument.

2.3. Electrochemical measurements

For the electrochemical testing of gC as anode material for Li ion battery, 75 % active material was blended with 15% polyvinylidene fluoride (PVDF) as binder and 10% conducting carbon with N methyl 2 pyrrolidone (NMP) solvent. This slurry was coated over a 0.009 μm thin copper foil and dried at 120 °C for 6 h in vacuum oven. A circular coin of 12 mm diameter was cut from this to employ as the anode material. The apparent density and loading density of the electrode are 0.48 g/cm^3 and 1.86 mg/cm^2 respectively. As reported by us earlier, that, higher reduction temperature leads to less wrinkled surface [24], to elucidate the role of wrinkles, gC-500, was also synthesized in the identical procedure but with higher hydrogen reduction temperature of 500 °C instead of 250 °C, and, was also shaped into 12 mm coin in the similar process to be tested as anode material. For comparison of the results with respect to the smooth surfaced multiwalled carbon nanotubes (MWNTs), circular testing coin was also made out of MWNTs, synthesized in the unchanged process using the same $MmNi_3$ hydride catalyst. Swagelok type two-electrode assembly with lithium foil as reference electrode were assembled inside argon (99.999%) filled glove box (mBRAUN, UNIlab; H_2O and $O_2 < 0.1$ ppm). Celgard 2400 separator dipped in lithium hexafluorophosphate ($LiPF_6$) (dissolved in ethylene carbonate and dimethyl carbonate (1:1)) electrolyte was used as both separator and electrolyte medium between the electrodes. Galvanostatic charge discharge studies were performed in an electrochemical workstation of Solatron analytical 1470E celltest system in the voltage range of 3 V–0.01 V (vs. Li^+/Li) for different current values. Electrochemical impedance spectroscopy (EIS) were done for the cells in the Solartron 1400 instrument by applying a sine wave of amplitude of 5 mV in the frequency range of 100 kHz to 0.01 Hz.

3. Results and discussion

Fig. 1 shows the comparative schematic of wrinkled gC with respect to smooth MWNTs and the proposed benefit of wrinkles on gC surface. At 250 °C in the hydrogen atmosphere, the rapid removal of oxygen containing functional groups from the graphite oxide leads to the formation of wrinkled graphene sheets. Acetylene gas, at the elevated temperature of 700 °C, decomposes to give carbon, which upon saturation over metal hydride catalyst grows as carbon nanotubes following the well-known vapor-liquid-solid mechanism. In this structure, GO produced graphene

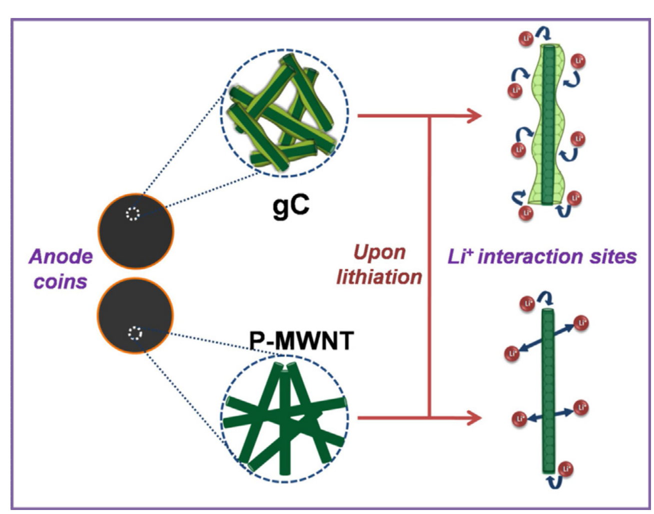

Fig. 1. Schematic representation of enhanced Li ion interaction sites for gC due to presence of wrinkles in comparison to MWNTs.