



Research Paper

In-situ Conversion of Multiwalled Carbon Nanotubes to Graphene Nanosheets: An Increasing Capacity Anode for Li Ion Batteries



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ABSTRACT

A unique in-situ morphology transition from multiwall carbon nanotubes (MWCNT) to graphene nanosheets (GNS) upon Li intercalation results in enormous increase in capacity of SnO₂/MWCNT composites anode during cycling. The anode capacity increases from 330 mAhg⁻¹ to 500 mAhg⁻¹ which is more than 50% of its initial capacity when cycled at a current density of 200 mA g⁻¹. Further when the sample is cycled at a high current density of 500 mA g⁻¹ the composite sample shows a stable capacity of 400 mAhg⁻¹ for 100 cycles which is attributed to the complete transition of MWCNT to GNSs as confirmed from the high resolution transmission electron microscope (HRTEM) images. First principles density functional theory calculations have been carried out to validate possibility of this morphological transition upon Li intercalation and the results agree well with the experimental findings.

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1. Introduction

Ever since the first commercial Lithium ion battery (LIB) was demonstrated by Sony Energetics in 1991, there has been a phenomenal growth of LIBs for multifarious applications [1–3] ranging from mobile phones to electric vehicles, space applications and recently in solar energy storage [1]. Conventional LIBs use graphite anode and LiCoO₂ cathode [3–6] in a non-aqueous electrolyte as components. Therefore, for next generation LIBs especially for use in clean energy storage and electric vehicles, further advancement in materials research is essential. The development of high performing cathode materials has already gained momentum with success viz., capacity enhancement from commercially used LiCoO₂ to lithium rich and double doped cobalt based materials with capacity greater than 200 mAhg⁻¹ [7–12].

Anode, like cathode is also a key component in determining the performance of LIBs; therefore, we felt it is apt to develop high performing anode materials for use in advanced LIBs. The fading of capacity during cycling which lessens the life time of the battery is

a key issue associated with the anode materials. Several approaches have been adopted to obtain stable capacity by synthesizing nanoparticles, use of porous structures and making composites with materials like carbon which can accommodate the volume changes during cycling and hence minimizing the fading [13–16].

In this context, it would be an out of box idea to investigate whether there is a possibility of increasing capacity with cycling. In any case, it would be interesting if cycling led to an increase in capacity rather than fading because upon usage the performance of the battery is being improved. The phenomenon of slight capacity rise upon cycling has been reported in some exceptional cases. For instance, the Sn@C nanocomposite synthesized via aerosol spray pyrolysis exhibited capacity increase during cycling at different current densities [17]. The reason for the capacity increase has been attributed to the reversible formation and decomposition of an organic polymeric gel like layer which forms a coating around the active materials and provides extra Li interfacial storage sites. Capacity rise during cycling has also been reported in carbon coated Fe₂O₃ hollow horns on CNT [18], mesoporous C/Sn composite [19] and SnO₂/graphene composite [20]. In all mentioned cases the capacity initially decreases to a low value and then gradually increases. The initial decrease in capacity is

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attributed to pulverization of metal particles during cycling which leads to loss of electrical connectivity between neighbouring particles. But as cycling progresses the metal particles are broken down into smaller particles by electrochemical milling effect and the smaller metal particles favours the reversible decomposition of Li_2O which leads to an increase in capacity.

In the present work, we demonstrate a free standing $\text{SnO}_2/\text{MWCNT}$ composite anode which exhibits increase in capacity of more than 50% with cycling with no initial fade. Even when the current rate is doubled there is no capacity fade, but an increase in capacity as compared to slower rate. The increase in capacity upon cycling is related to the in-situ formation of graphene nano sheets (GNS) by the opening up of MWCNT. The exact mechanism for the increase in capacity is depicted by HRTEM, Raman and theoretical validation. Such advanced promising anode materials opens up a new area of research.

2. Experimental

2.1. Synthesis of MWCNTs

MWCNTs were synthesized using the in-house chemical vapour deposition (CVD) set up at CSIR-NPL, India. 3.5 g of ferrocene dissolved in 40 ml toluene was injected into the CVD quartz tube maintained at a temperature of 750°C in argon atmosphere, at a rate of 10 ml/hour. The details of experimental set-up are given elsewhere [21]. MWCNTs formed were collected and well characterized as discussed further.

2.2. Synthesis of $\text{SnO}_2/\text{MWCNT}$ composites

MWCNTs were dispersed in ethylene glycol (Merck Ltd) by ultra-sonication for 3 h. 0.1 M solution of stannous chloride ($\text{SnCl}_2 \cdot \text{H}_2\text{O}$; Qualigens) was added to the dispersed MWCNT drop by drop with constant magnetic stirring. It was then refluxed in air at 150°C for 4 h. The process of refluxing allows proper mixing of the components. Refluxing was followed by washing with sufficient amount of triple distilled water and then drying to obtain $\text{SnO}_2/\text{MWCNT}$ composites.

2.3. Fabrication of free standing anode from MWCNTs and $\text{SnO}_2/\text{MWCNT}$ composites

MWCNTs as well as the composite were well dispersed in iso-propyl alcohol and then filtered through a filter paper using vacuum filtration giving free standing film/paper which can be peeled off after drying. 20 cm x 20 cm size papers were made by vacuum filtration, each of MWCNT and $\text{SnO}_2/\text{MWCNT}$. These free-standing films can be used directly as a flexible electrode material in a cell without the need for a binder and a Cu foil as current collector. The addition of electrical conducting material can also be avoided due to the high electrical conductivity of MWCNTs. Free-standing film electrodes are attractive for basic electrochemical characterization because of their ease of handling, and most importantly due to the absence of the binder and copper current collector. Also there is a decrease in dead weight of the cell as well as an increase in the usable capacity. Fig. 1 depicts the scheme of fabrication of the free standing anode.

2.4. Characterization

Thermal gravimetric analysis (TGA) of the prepared free standing MWCNT and $\text{SnO}_2/\text{MWCNT}$ samples has been carried out on TGA/DSC Mettler Todedo to estimate the loading amount of SnO_2 in the composites. The experiments were carried out in air at $10^\circ\text{C}/\text{min}$ rate up to 1000°C . The morphology and the structural details of the composite samples were studied with the help of scanning electron microscopy (SEM), field emission (FE) SEM and HRTEM. The X-ray diffraction examination of the samples has been performed on Rigaku powder X-ray diffractometer model: 2KW using $\text{Cu-K}\alpha$ radiation at a scan rate of $0.1^\circ/\text{s}$. Raman spectroscopy has been carried out at room temperature and in air using a Renishaw InVia Reflex Micro Raman spectrometer equipped with the CCD detector. Green laser (excitation line 514 nm at 2.5 mW power) was used to excite the samples.

Anode discs of 18 mm diameter were cut from the free standing $\text{SnO}_2/\text{MWCNT}$ and MWCNT paper for the fabrication of LIB. Coin type cells were assembled using free standing anode, lithium foil counter electrode, a separator (polypropylene film) and organic

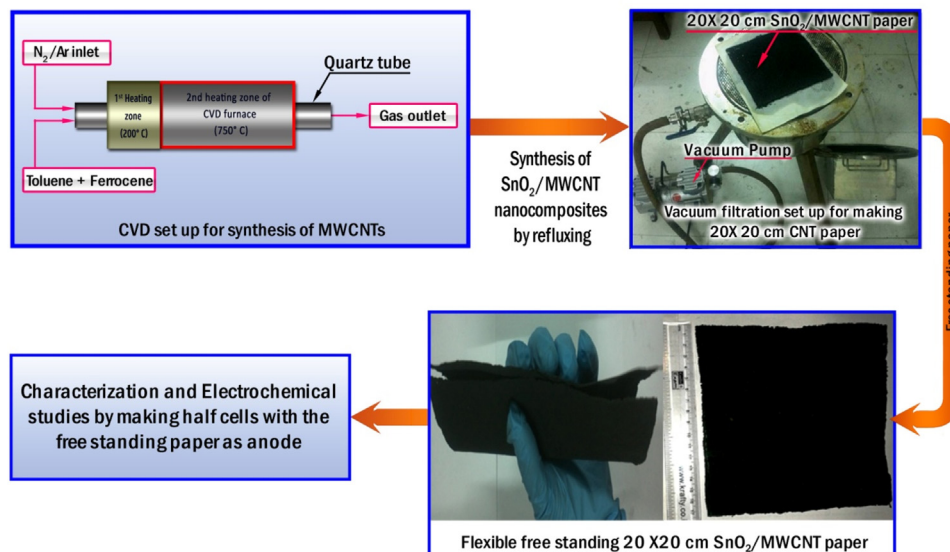


Fig. 1. Experimental set-ups for making of free standing anode for Li ion batteries.

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