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Selenium containing Tube-in-Tube carbon: A one dimensional carbon frame work for selenium cathode in Li-Se battery

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ABSTRACT

MWCNT encapsulated by highly porous carbon, also called as Tube-in-Tube carbon (TTC), obtained from hard template assisted synthesis method acts as an efficient host for Se cathode in Li-Se battery. One dimensional nano structured TTC with a high pore volume of 2.167 cc/g and an appreciable surface area of 1131 m^2/g is capable of accommodating as high as 70 wt% Se. Notably, 50 wt% Se@TTC delivers an initial capacity of 625 mAh/g at C/5 rate and an acceptable progressive capacity of 403 mAh/g up to 800 cycles. Further, 55% of the initial capacity is retained up to 800 cycles under 2C rate. It exhibits 254 mAh/g at 10C rate and an insignificant decay of 0.01% per cycle at 1C rate for 4000 cycles. On the other hand, 60 wt% Se@TTC exhibits superior capacity behaviour than 50 wt%. Se loaded cathode up to 3C rate and a moderate capacity of 190 mAh/g at 10C rate. Based on the demonstration of excellent cycleability, superior reversibility and rate capability, TTC is recommended as a promising host for Se cathode in Li-Se batteries. The encouraging electrochemical performance of Se@TTC could be attributed to the synergistic effect of MWCNT and porous nature of carbon.

1. Introduction

The rapidly depleting fossil fuels and the looming threat on environmental pollution pose an ever pressing need for the development of high capacity and long lasting energy storage device for application in portable devices and electric vehicles [1,2]. Despite the attractive features of lithium-sulfur (Li-S) batteries like high theoretical energy density and capacity, the practically achievable energy density and cycle life are limited even after massive R&D efforts, which impede its practical application [3,4]. Next to sulfur, selenium is considered as an alternative potential electrode for electric vehicle and smart grids due to its inherent advantages over Li-S system [5]. High theoretical energy density (1627 Wh/kg *vs.* Li) of Li-Se system mainly arises from the two electron transfer involving electrochemical reaction and possesses high theoretical gravimetric capacity of 675 mAh/g and volumetric capacity of 3253 mAh/cm^3 based on the reversible redox reaction $Se + 2Li^+ + 2e^- \leftrightarrow Li_2Se$ [5]. Lesser theoretical gravimetric capacity of Se than S is offset by its comparable volumetric energy with that of S for portable device applications. Se, the d-electron containing element, has an electronic conductivity in the order of 10^{-5} S/cm, which is approximately 20 times higher than that of elemental sulfur, thus indicating the possibility of higher utilization of active material and faster electrochemical reaction. Moreover, weaker shuttle effect due to limited dissolution of polyselenides favours the long term cycleability, which is limited in Li-S system due to the high degree of polysulfide dissolution [5].

Nevertheless, Li-Se system also suffers from battery performance poisoning characteristics analogous to S to some extent, such as low Se utilization due to certain degree of polyselenide dissolution and the semiconducting nature of Se, especially when bulk Se is employed as cathode [5]. In order to improve the electrochemical performance, uniform distribution and confinement of Se in a conductive network is essential to restrain the electrochemically active material in the cathode side throughout the cell operation and to facilitate electron and ion transport. Towards this direction, confinement of Se in porous carbon based matrix is a promising strategy [6–11]. Pioneer work has been conducted by Abouimrane et al. [5] in this regard that Se can be exploited as a potential cathode material. But lower utilization of Se was observed, especially when it was intimately mixed with CNT. On the other hand, it is found from this study that CNT improves the conductivity, but the absence of porous structure to restrain the polyselenide and the loss of integrity between CNT and Se/Li_2Se

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during cycling is responsible for lower utilization of Se. Of late, various porous carbon strategies have been utilized to realize promising improvement in the performance of Se cathode in Li-Se systems. Se impregnated ordered mesoporous carbon [6] and hierarchical micro/mesoporous carbon sphere [7–9], reduced graphene oxide encapsulated Se nanoparticles [10] and three dimensional framework of CNT/Se sandwiched between graphene sheets [11] are few examples of carbon based strategy reported for Se confinement. It is reported [6] that impregnated Se in the form of cyclic Se_8 in the pores of carbon is converted into chain like Se_n molecule after the first discharge/charge cycle and the same is maintained throughout cycling. In addition, the chain like Se_n molecule is reported to interact with carbon in an effective manner to ensure better utilization of active material and realization of improved capacity behaviour.

Of the reports available in the literature, it is found that amorphous carbon with predominant sp^3 hybridization suffers from inferior conductivity and poor rate capability behaviour [12,13]. On the other hand, CNT and graphene based sp^2 hybridized carbon matrices upon impregnation of Se suffer from poor contact between C and Se which in turn results in the poor integrity of electrode upon extended cycling [5,10]. As a result, mesoporous carbon encapsulated MWCNT [14,15], otherwise known as TTC has been exploited in the present study to accommodate Se to form a composite with synergistic advantages of MWCNT and the porosity driven higher utilization of active material. It is well known that MWCNT offers excellent electronic conductivity, good flexibility, one-dimension structure, high aspect ratio and better chemical/thermal stability, which are believed to impart inherent advantages to the resultant Se@TTC composite.

With this perception, various amount of Se has been impregnated into the mesoporous carbon encapsulated MWCNT (labelled as Tube-in-Tube carbon (TTC)) to its molecular level by melt diffusion strategy with a view to identify the optimum Se loading. In the present case, MWCNT (core) backbone provides the facile electron transfer path and the surrounding porous carbon (shell) precludes the loss of active material. Further, the shorter Li-ion diffusion length facilitated by the one-dimensional nanostructure of TTC greatly improves the utilization of active material even at ultra high rates and ensures the long term stability of cathode under the influence of different current rates with an excellent Coulombic efficiency, closer to 100%. The void space between the core and shell in combination with the larger pore volume of mesoporous shell of TTC offers better tolerance against the stress that arises due to the volume expansion/contraction associated with lithiation/delithiation of Se cathode during cycling process. Further, recommendation is made for high rate and long term cycleability behaviour in terms of amount of Se loaded in TTC and the details are discussed in this communication.

2. Experimental sections

2.1. Synthesis of Tube-in-Tube carbon

All the chemicals used are of analytical grade. 1 g MWCNT (Dia: 10–25 nm, length: 10–50 μm from ILJIN Nanotech Co-Ltd) in 65 wt % of aqueous HNO_3 (Merck) was sonicated for 30 min followed by reflux at 140 °C for 12 h to functionalize the same. About 110 mg of F-MWCNT was dispersed in a mixture of 160 ml of ethanol (Hayman) and 10 ml of deionised water (D.I. H_2O, with an electrical resistivity of 18.2 MΩ) and sonicated for 30 min. To the content, 2 ml of aqueous ammonia (25–28 wt % Acros Organics) and 1.36 ml of TEOS (Sigma Aldrich) were added and stirred for 24 h. Then, the mixture containing 0.8 ml TEOS and 0.53 ml octadecyltrimethoxysilane (C_{18} TMS, TCI Chemicals) was added drop wise into the solution and allowed to stir for 8 h. The as obtained product was repeatedly washed with ethanol and D.I. H_2O separately and dried at 80 °C overnight. 1 g of dried product was re-dispersed into 60 ml of H_2O_2 (Merck) and stirred for 15 h and filtered. Filtered product was again dispersed into 20 ml of D.I. H_2O containing 0.8 ml of H_2SO_4 (Sp. Gr.: 1.84, Fisher Scientific) and dried with a heating sequence of 100 °C for 5 h and 160 °C for 15 h. The powder thus obtained was carbonized at 800 °C for 3 h with a heating ramp rate of 3°/min and subsequently etched with 5% HF solution (Rankem) to remove silica. Selenium (Acros Organics) loaded TTC (denoted as TTC/Se-X where X = 50, 60, 70 wt% of selenium) was obtained by melt diffusion strategy. Required amount of selenium was mixed with TTC and kept at 260 °C for 12 h in a closed vessel to obtain such TTC/Se-X composites. For comparison purpose, 50:50 wt% physically mixed TTC and Se (labelled as TTC-Se-50) and 50:50 wt% of MWCNT: Se were also prepared by similar heating procedure to understand the advantages of TTC over MWCNT.

2.2. Material characterization

As prepared TTC and TTC/Se-X composites were subjected to the following investigations. XRD was recorded with a Bruker D8 Advance X-ray diffractometer (XRD) using Ni-filtered Cu Kα radiation. TGA, Raman spectral studies and electrical conductivity of TTC and TTC/Se-X were performed using NETZSCH STA 449F3, Renishaw inVia Raman Microscope using He–Ne LASER and four probe setup (SES Instrument Pvt Ltd) respectively. N_2 adsorption/desorption isotherm was obtained from Quantachrome Instruments version 3.01 and XPS results from a MULTILAB 2000 Base system. Elemental mapping and/or morphology were studied using Gemini Field Emission Scanning Electron Microscopy (FESEM), Tecnai 20 G2 (FEI make) and HR-TEM images and STEM EDX mapping of the samples were captured using Jeol Jem 2100 TEM analyser.

2.3. Electrode fabrication and electrochemical characterization

To prepare the electrode, TTC/Se-X composites were mixed with super-P carbon and sodium CMC binder (both from Alfa Aesar) to form a slurry, which was coated on an aluminium foil and dried at 60 °C overnight. Electrochemical performance of TTC/Se-X cathodes were evaluated using 2032 coin cell (M/s. Hohsen Corporation) consisting of TTC/Se-X as working electrode, punched out from the coated foil and lithium metal as counter and reference electrode separated by polypropylene. 1 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v) (Sigma Aldrich) serves as the electrolyte. Cyclic Voltammetry (CV) and impedance measurements were carried out using a VMP3 multichannel potentiostat–galvanostat system (Biologic Science Instrument). Charge–discharge studies were carried out using Arbin charge–discharge cycler/VMP3 multichannel potentiostat–galvanostat system.

3. Result and discussion

3.1. Physical characterization

Fig. 1 shows the step by step strategy involved in the synthesis of TTC. First, solid SiO_2 layer was coated over the functionalized MWCNT and then porous SiO_2 was coated over the solid SiO_2 layer based on modified stober method [14,15]. Octadecyltrimethoxysilane (C_{18} TMS) was used as a porogen to obtain porous SiO_2 coating and finally C_{18}TMS serves as carbon precursor. Carbonization of carbon precursor containing SiO_2 layer/SiO_2 layer/MWCNT framework was carried out after chemical activation. Finally, Se was