SnO and SnO.CoO nanocomposite as high capacity anode materials for lithium ion batteries

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Abstract

We prepared SnO nanoparticles (SnO-S) and SnO.CoO nanocomposites (SnO.CoO-B) as anodes for lithium ion batteries (LIBs) by chemical and ball-milling approaches, respectively. They are characterized by X-ray diffraction and TEM techniques. The Li-storage performance are evaluated by galvanostatic cycling and cyclic voltammetry. The SnO-S and SnO.CoO-B showed improved cycling performance due to their finite particle size (i.e. nano-size) and presence of secondary phase (CoO). Better cycling stability is noticed for SnO.CoO-B with the expense of their reversible capacity. Also, addition of carbon nanotubes (CNT) to SnO-S further improved the cycling performance of SnO-S. When cycled at 60 mA g^{-1} , the first- cycle reversible capacities of 635, 590 and 460 (± 10) mA h g^{-1} are noticed for SnO-S, SnO@CNT and SnO.CoO-B, respectively. The capacity fading observed are 3.7 and 1.8 mA h g^{-1} per cycle for SnO-S and SnO@CNT, respectively; whereas 1-1.2 mA h g^{-1} per cycle for SnO.CoO-B. All the samples show high coulombic efficiency, 96-98% in the range of 5-50 cycles.

Key words: Oxides; Chemical synthesis; Transmission electron microscopy; Electrochemical properties; Energy storage.

1. Introduction

Nanomaterials are widely studied for different applications due to their improved properties. These materials are tailored to different sizes and structures to improve their performance [1-4]. They are also found to be used extensively as electrode materials for energy storage, for example in lithium ion batteries (LIBs) and super capacitors [5-10]. Due to their finite size ($\sim$ nanometer) and high surface area, they are beneficial for energy storage devices. They show fast Li- ion diffusion due to their reduced particle sizes to few order of nanometer ($\tau = L^2/D_{Li}$) [10]. Graphite is mostly being used as negative electrode material for commercial LIBs. It is excellent as negative electrode material due to its excellent cycling performance in terms of long cycle life. However, it suffers from low specific capacity (Theoretical: 372 mA h g^{-1}) and hence low specific energy. The reversible reaction involves intercalation/de- intercalation of maximum up to 1 Li^+ per C_6 and as a result ended up with low specific capacity. However, carbon in the form of CNTs and graphene are also employed as negative electrode for LIBs and they delivered higher specific capacity compared to graphite and explained as storage of more than 1 Li^+ [11-13]. The high surface area is the barrier for their practical use as negative electrode materials, as the volumetric energy density is very poor, as well as they can decompose electrolyte when discharge to low voltage. Transition metal oxides are opted as the alternative to graphite as possible electrode materials. They can deliver high reversible specific capacity based on ‘conversion reaction’ ($\text{MO} + 2 \text{ Li} \leftrightarrow \text{M} + \text{Li}_2\text{O}$; $\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Fe}$ etc.) [14- 17]. Group of Tarascon first reported the conversion reaction mechanism in case of transition metal oxides, where they undergo structural transformation and formation of metal nanoparticles ($\sim 2\text{-}3 \text{ nm}$) embedded in amorphous Li_2O [14]. In spite of their high specific capacity, they suffer from high operating voltage and large voltage hysteresis.

Sn- based oxides and its intermetallic are widely used as negative electrode materials due to their high theoretical capacity. The Sn forms alloy with Li to form Li_xSn ; $0 \leq x \leq 4.4$, as a result shows high theoretical capacity (994 mA h g^{-1}). The low alloying/de-alloying voltage and low voltage hysteresis are two major advantages of Sn- based electrode materials. However, they suffer from large volume change ($\sim 300\%$); as a result severe capacity degradation is noticed. The large volume change causes electrode disintegration and hence electrical contact is lost from current collector. In order to overcome such problem of large volume change, nano-structuring of electrodes [18, 19], precise carbon coating [20, 21] and introducing secondary phases [22- 26] approaches to Sn based electrode materials were adopted. It was noticed that after such treatment, they showed better capacity retention. SnO and SnO_2 are well studied as negative electrode materials for LIBs. They show high reversible capacity ($\sim 875 \text{ mA h g}^{-1}$ for SnO and 782 mA h g^{-1} for SnO_2 considering $\text{Li}_{4.4}\text{Sn}$ reaction) and are also easy to prepare. However, SnO and SnO_2 suffer from capacity degradation due to large volume change associated during cycling. These issues were addressed with various approaches. Tian et al. prepared a SnO_2/C composite of ultra-small SnO_2 nanoparticles ($\sim 6 \text{ nm}$) by a hydrothermal method. They showed a reversible capacity of 839 mA h g^{-1} at 200 mA g^{-1} after 217 cycles and 713 mA h g^{-1} at 800 mA g^{-1} after 378 cycles [27]. Hu et al. reported the synthesis of SnO nanoplates by flame synthesis and showed a high initial reversible capacity of 945 mA h g^{-1} at 100 mA g^{-1} . They explained as nanosize of SnO is beneficial for high reversible capacity and also better capacity retention [28]. Zhang et al. reported the synthesis of SnO ultrathin nanosheets by hydrothermal process and showed a high reversible capacity of 559 mA h g^{-1} after 20 cycles. They claimed unique structure of SnO is responsible for better cycling performance [29]. Tian et al. prepared the $\text{SnO}_2/\text{TiO}_2/\text{C}$ hollow microsphere by facile hydrothermal strategy. They showed excellent cycling performance of $\text{SnO}_2/\text{TiO}_2/\text{C}$ due to the hollow structure and presence of TiO_2 as secondary

phase. The composite showed stable capacity of $\sim 500 \text{ mA h g}^{-1}$ for 500 cycles at 200 mA g^{-1} [30]. Liu et al. prepared amorphous nanomembrane of SnO_2 and showed a high capacity of 854 mA h g^{-1} stable for 1000 cycle at 1600 mA g^{-1} . They explained the superior performance of SnO_2 is due to the structural features of amorphous SnO_2 [31]. Earlier, our group reported the preparation and Li- storage performance of $\text{M}_{1/2}\text{Sb}_{1/2}\text{SnO}_4$ ($\text{M} = \text{V}, \text{Fe}, \text{In}$) [22-25], $\text{SnO}(\text{VO}_x)$ nanocomposite [26] and Sn- hollandites $\text{K}_2\text{M}_2\text{Sn}_6\text{O}_{16}$ ($\text{M} = \text{Co}, \text{In}$) [32] and showed improved cycling performance due to the presence of secondary phases.

In the present study, we report the Li storage of chemically prepared SnO (SnO-S) nanoparticles and ball milled SnO.CoO (SnO.CoO-B) nanocomposite, respectively and compared to that of the commercial micron- size SnO (SnO-C) and ball milled SnO (SnO-B). The SnO nanoparticles are prepared at relatively low temperature in order to limit the growth of particles and also to stop the transformation of SnO to SnO_2 . The SnO-S and SnO.CoO-B showed improved cycling performance when they are prepared to nano-size and also the presence of secondary phase (CoO). We also notice further improvement in cycling of SnO-S when carbon nanotube (CNT) is introduced during electrode preparation. The reduction in particle size and presence of secondary phase improved the cycling performance of SnO compared to that of SnO-C and SnO-B. The SnO.CoO-B showed almost a stable capacity until 50th cycle, whereas low specific capacity is observed as CoO is electrochemically inactive in this potential window. SnO-S and SnO@CNT showed high reversible capacity with low capacity fading until 50th cycle. The coulombic efficiency for all is 96-98 % after 5th cycle.

2. Experimental

2.1. Synthesis of SnO nanoparticles and SnO.CoO nanocomposite

For the synthesis of SnO nanoparticles, the chemicals were used as received without further purification. The $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.02 M; 4.51g) was mixed with NaOH (0.04 M; 1.6 g)

and ground in a mortar. During grinding, NaCl was added to the mixture to prevent the growth of particles as well as agglomeration. The mixture was collected and heated inside a tube furnace (Carbolite, UK) to an elevated temperature of 200 °C in flowing Ar- gas for 3 hours. After heating, the powder was collected and ground to fine powder followed by washing in distilled H₂O and drying at room temperature. The experimental procedure for the synthesis was followed from literature with some modifications [33]. The SnO nanoparticles prepared by chemical route are written as SnO-S hereafter.

For the synthesis of CoO.SnO nanocomposites, different compositions of SnO to CoO were prepared by high energy ball milling (HEB) under inert condition. Mechanical ball-milling is one of the effective methods to prepare various nanomaterials and their composites for improved energy storage performance [34-36]. The commercial SnO (Acros Organics, 98%) and CoO were used as starting materials for ball milling. Appropriate amount (~2.5 g) was weighed keeping different molar ratios of SnO to CoO and transferred to stainless steel vial inside in an Ar-filled glove box (MBraun, Germany). The vial was set for HEB at a speed of 1,400 rpm using Spex, 8000D, USA instrument. The ball milling was carried out using stainless steel balls maintaining ball-to active mass ratio of 4:1 for 18 h, in three steps of 6 h each, to avoid significant rise in temperature inside the vial. The detailed experimental procedure is similar to our previous reports [26, 32]. For the sake of convenience, the nanocomposites prepared by HEB are, $\frac{3}{4}\text{SnO} \cdot \frac{1}{4}\text{CoO}$ and $\frac{2}{3}\text{SnO} \cdot \frac{1}{3}\text{CoO}$. The CoO used for the synthesis was prepared by carbothermal reduction at 750 °C in Ar- gas atmosphere. The SnO.CoO nanocomposite prepared by ball milling is written as SnO.CoO-B hereafter.

The structure and morphology of SnO-S and SnO.CoO-B were analyzed by X-ray diffraction (XRD) using Philips X'PERT MPD unit (Cu K_α radiation) and high resolution

transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED) (JEOL JEM 3010 operating at 300 kV). For electrochemical measurement, electrodes were prepared from active materials (Here, SnO-S, SnO.CoO-B etc.), carbon black (Super P, MMM) and binder (PVDF) in the weight ratio of 70-15-15. In case of SnO@CNT electrode preparation, the CNT was used in place of Super P carbon black. They are mixed well by grinding. Homogeneous slurry was prepared using N-methyl-pyrrolidinone (NMP) as solvent. Thick film of 15 μm was prepared by coating the slurry onto the etched Cu- foil (10 μm , Alpha Industries Co. Ltd., Japan) using doctor bladed technique followed by drying inside the vacuum to evaporate the NMP. The electrodes were cut to disc of $\phi = 16$ mm before assembling the cells. Coin cells (2016) were fabricated inside the Ar- filled glove box (MBraun, Germany). The level of H_2O and O_2 was maintained < 1 ppm inside the glove box. The Li- metal (Kyokuto Metal Co., Japan) was used as counter electrode. The glass microfiber filter (GF/F) (Whatman Int. Ltd, Maidstone, England) was used as the separator and 1M LiPF_6 dissolved in ethylene carbonate (EC) + diethyl carbonate (DMC) in the ratio of 1:1 volume (Merck) as the electrolyte. The electrode preparation and cell fabrications are discussed in detailed in our previous reports [37-40]. The cells were aged for 12 h prior to testing in order to ensure complete percolation of electrolytes into the electrodes. The electrochemical performances were evaluated by both galvanostatic and cyclic voltammetry (CV) modes using galvanostatic cycler (model SCN, Bitrode, USA) and Macpile II system; Biologic, France instruments at room temperature, respectively.

3. Results and Discussion

3.1. Structure and morphology

The structures of SnO-S and SnO.CoO-B nanocomposite were analyzed by using XRD measurement. Fig.1a shows the XRD pattern of SnO-S nanoparticles prepared by solid state reaction at low temperature. The pattern shows the pure phase formation of SnO and

belonged to tetragonal crystal structure with I4/mna space group (PDF: 00-001-0902) [28, 29]. The peaks observed at 18.3°, 30.0°, 33.4° and 37.2° can be assigned to the diffraction planes of SnO(001), SnO(101), SnO(110) and SnO(002), respectively. Fig.1b shows the XRD patterns of SnO-B and SnO.CoO-B nanocomposite. The XRD pattern of SnO-B is given for comparison. The characteristic peaks observed for SnO-B can be assigned to SnO₂ (PDF: 00-041-1445) and Sn (PDF:00-004-0673). It is noticed that the SnO is unstable to high energy ball milling and disproportionated to SnO₂ and Sn (Eqn.2). This is due to the thermodynamically instability of SnO, which disproportionates to SnO₂ and Sn as per Eqn.2.

The detailed mechanism is discussed in the previous report [26, 41]. The XRD pattern of SnO.CoO-B shows the mixture of SnO₂ (PDF: 00-041-1445), SnO (PDF: 00-001-0902) and in-situ formed Co (PDF: 00-004-1507). The assigned (*h k l*) values are due to SnO₂ characteristic peaks (Fig.1b). During ball milling, the SnO decomposed to SnO₂, Sn and further reduction of CoO was noticed. The freshly formed Sn possibly reduced CoO to form SnO and Co, which is confirmed from the diffraction pattern of SnO.CoO-B nanocomposite (Fig.1b). This reaction mechanism is also thermodynamically favorable, as the Gibbs' free energy of formation is negative ($\Delta G = -47$ kJ/mol) for the forward reaction (Eqn.3).

The morphology of SnO-S and SnO.CoO-B was analyzed by using TEM. Fig. 2a-d show the TEM micrographs of SnO-S. It can be clearly seen from Fig.2a-c that nanoparticles of SnO of particle size ranging from 20-30 nm (even some particles are smaller than 20 nm) are well dispersed without much agglomeration. No definite morphology for SnO nanoparticles is noticed. The dispersion of these SnO nanoparticles is due to the addition of NaCl which prevented the agglomeration of SnO nanoparticles during synthesis. The HR-TEM lattice image is shown in Fig. 2 d, where the d- spacing (inter planar distance) of the

plane is $2.96 (\pm 0.02) \text{ \AA}$ and this corresponds to the Miller indices (101) of SnO (Fig. 1a). The electron diffraction pattern (Inset of Fig.2a) shows the formation of pure phase SnO and corroborates to XRD pattern (Fig.1a). The diffraction pattern shows highly resolved concentric rings and some bright spots indicating the nanocrystalline nature of SnO. The TEM micrographs of SnO.CoO-B nanocomposite are given in Fig. 2e, f. It is noticed that the nanoparticles of 15-20 nm are agglomerated to form large particles. They did not show definite morphology. The TEM image of SnO.CoO-B (Fig. 2 e,f) confirms the reduction of particle size to nanometer scale due to high energy ball milling. Such effect is also observed in the XRD pattern (Fig.1b) reflected from the broadening of XRD peaks. The d- values calculated from Fig.2f refer to the SnO₂ and Co phases in the SnO.CoO-B nanocomposite. The calculated d- values are 3.38, 2.67, 2.38 and 2.09 (± 0.04) $\text{\AA}$, which correspond to (110), (101) and (200) due to SnO₂; whereas (111) due to Co- metal, respectively.

3.2. Electrochemical properties

3.2.1. Cyclic voltammetry of SnO-S and SnO.CoO-B

Fig. 3a shows the cyclic voltammograms (CVs) of SnO-S for 1-6 cycles at $58 \mu\text{V s}^{-1}$ in the voltage window of 0.005-1.0 V. The upper cut-off voltage was selected based on formation/decomposition of Li_xSn ($0 \leq x \leq 4.4$), restricting the reversible formation of SnO during charge process to minimize the volume change and hence, stabilization of capacity fading [15]. It can be seen from the first discharge (cathodic) sweep, no voltage plateaus are noticed until 1.0 V. Thereafter, two intense and broad voltage peaks are noticed when discharged further to 0.005 V. The voltage peak noticed at ~ 0.75 V is due to the structural transformation of SnO to nano-Sn and amorphous Li₂O [Eqn.4]. Whereas the voltage peaks noticed at ~ 0.27 and 0.17 V are due to the formation of alloy Li_xSn ($0 \leq x \leq 4.4$) [Eqn.6] and solid electrolyte interface (SEI) [14, 15, 41-44].

During the subsequent charging, the CV shows a high intense peak at ~0.52 V and a shoulder peak at ~0.65 V, which are due to the de-alloying of Li_xSn (formed in the previous discharge process) [Eqn.6], indicating that the de-alloying occurred in stages [23]. The CVs from 2-6 cycles represent the reversible formation/or de-composition of Li_xSn . With increase in the cycle number, the area under the I/V curves decreased, indicating capacity degradation.

Fig. 3b shows the CVs of SnO.CoO-B nanocomposite prepared by ball milling approach in the voltage window of 0.005-0.8 V at a scan rate of $58 \mu\text{V s}^{-1}$. It was noticed that during ball milling of SnO and CoO, the major product SnO_2 was formed along with Co and SnO (less than 5 wt.% and hence neglected compared to SnO_2) as secondary phases (Fig1b). The CVs noticed in Fig.3b are due to typical SnO_2 . During first discharge, the CV profile shows a high intense peak at ~0.9V due to the structural transformation of SnO_2 to Sn and Li_2O [Eqn.5] and followed by a broad voltage peak at ~0.17 V. The later voltage plateau corresponds to the Li_xSn and SEI formation [14, 15, 41-44]. In the subsequent charging, the CV shows a high intense peak at ~0.5 V, indicating the de-alloying of Li_xSn [Eqn. 6]. The CVs from 2-6 cycles overlap each other indicating excellent reversibility. The area under the I/V curves remained same with increase in cycle number indicating stable cycling performance.

3.2.2. Galvanostatic cycling of SnO-S, SnO@CNT and SnO.CoO-B nanocomposite

The Li- storage performance of SnO-S and SnO@CNT was evaluated by galvanostatic cycling in the voltage window of 0.005-0.8V vs. Li at a current density of 60 mA g^{-1} and the discharge- charge profiles for selected cycles are shown in Fig.4. The voltage vs. capacity profiles of SnO-S are shown in Fig.4a, b for 1st, 2nd, 10th and 50th cycles, respectively. In the first discharge, it shows a voltage plateau at ~ 1.0 V, which corresponds

to a discharge capacity of $\sim 404 \text{ mA h g}^{-1}$ (consumption of ~ 2.03 mole of Li per formula unit of SnO). This corresponds to the structural transformation of SnO to Sn and Li_2O (Eqn.4). Thereafter, a sloping profile is noticed until 0.005V. The first discharge capacity noticed at the end of 0.005V is $1725 (\pm 10) \text{ mA h g}^{-1}$ (~ 8.66 moles of Li). The total first discharge capacity is due to the structural transformation of SnO and followed by formation of Li_xSn alloy and SEI layer. From Eqns. 4 & 6, it is expected that theoretically 6.4 moles of Li can be consumed during first discharge. However, ~ 8.66 moles of Li were consumed at the end of first discharge with excess of ~ 2.26 moles. The extra capacity is due to the formation of SEI layer [14, 15, 41-44]. In the subsequent charging to 0.8 V, it shows a total capacity of $635 (\pm 10) \text{ mA h g}^{-1}$ (~ 3.2 moles of Li) with first cycle coulombic efficiency as low as $\sim 37\%$ (Fig.6c). The reversible charge capacity is due to the de-alloying of Li_xSn (Eqn.6). Fig.4b shows the discharge- charge profiles from 2- 50 cycles. It can be seen that these discharge-charge profiles are due to the alloying/de-alloying reaction of Sn with Li. The reversible capacity observed at the end of 50th cycles is $450 (\pm 10) \text{ mA h g}^{-1}$ (~ 2.26 moles of Li). With increase in cycle number, the capacity fading is observed with 3.7 mA h g^{-1} per cycle. The coulombic efficiency at the end of 50th cycle is noticed, as 98%. The galvanostatic discharge-charge profiles of SnO@CNT at 60 mA g^{-1} in the voltage window of 0.005-0.8 V vs. Li are shown in Fig.4c,d for 1st, 2nd, 10th and 50th cycles, respectively. It is noticed that similar discharge- charge profiles are observed for SnO@CNT. However, the observed capacities values are slightly different compared to that of SnO-S. It shows first discharge capacity of $1810 (\pm 10) \text{ mA h g}^{-1}$ (~ 9.09 moles of Li), whereas first charge capacity is $590 (\pm 10) \text{ mA h g}^{-1}$ (~ 2.96 moles of Li) with first cycle coulombic efficiency of 33%. Such low coulombic efficiency for SnO@CNT compared to that of SnO-S is possibly due to the presence of CNT of high surface area, which consumes excess Li during discharge reaction. At the end of 50th cycles, it shows a reversible capacity of $500 (\pm 10) \text{ mA h g}^{-1}$ (~ 2.51 moles of Li) with capacity

fading of 1.8 mA h g^{-1} per cycle. The capacity retention is better compared to SnO-S due to the presence of CNT, which provide additional electronic conductivity as well as buffer the volume change.

The galvanostatic discharge- charge cycling profiles of SnO.CoO-B nanocomposite in the voltage range of 0.005-0.8 V vs. Li and at a current density of 60 mA g^{-1} are shown in Fig. 5a, b. The capacity is calculated w.r.t. the total weight of the composite. The observed capacity is due to reversible reaction of Sn with Li in this voltage window. However, the voltage vs. capacity profiles of $\frac{3}{4} \text{ SnO} \cdot \frac{1}{4} \text{ CoO}$ composition is given as they are similar to that of $\frac{2}{3} \text{ SnO} \cdot \frac{1}{3} \text{ CoO}$ composition. It was noticed that during ball milling, the major phases formed are SnO_2 with Co- metal and SnO as secondary phases (Fig.1b). However, Co- metal does not contribute to the observed capacity (since Co is inactive matrix element), whereas the discharge- charge profiles are due to the SnO_2 . During the first discharge process, a sloping profile is noticed with a prominent voltage plateau at $\sim 0.9 \text{ V}$. This voltage plateau is due to the structural transformation of SnO_2 to Sn and Li_2O (Eqn.5). This is followed by a sloping profile until the discharge voltage, 0.005V with no major voltage plateaus noticed. The first discharge capacity observed at the end of 0.005 V is $1395 (\pm 10) \text{ mA h g}^{-1}$. The first charge capacity when cycled to 0.8V is $460 (\pm 10) \text{ mA h g}^{-1}$, which is due to the de-alloying of Li_xSn formed during the previous discharge, and is reflected by the voltage plateau noticed at $\sim 0.5\text{V}$. The SnO.CoO-B shows first cycle coulombic efficiency of 33%. Such low coulombic efficiency is due to the irreversible Li stored in the defects formed due to high energy ball milling. The discharge-charge profiles from 2-50th cycles (Fig.5b) are due to the alloying/de-alloying reaction of Sn. At the end of 50th cycle, the reversible charge capacity noticed is $400 (\pm 10) \text{ mA h g}^{-1}$ with 50th cycle coulombic efficiency as high as 98%. The capacity fading noticed for SnO.CoO-B nanocomposite is almost negligible, which is 1.2 mA h g^{-1} per cycle. The differential capacity vs. voltage profiles of SnO.CoO-B extracted from

their discharge/charge profile are shown in Fig.5c,d for 1st, 2nd and 50th cycles, respectively. They show the voltage plateaus which are not clearly noticed in discharge-charge profiles. These voltage plateaus resembles with the plateaus noticed during CV measurement (Fig.3b).

The capacity vs. cycle number plots for SnO-C, SnO-S, SnO-B and SnO@CNT up to 50 cycles (22 cycles for SnO-C) at 60 mA g⁻¹ current density are shown in Fig.6a. In the present study, we compared the Li- cycling performance of SnO-S and SnO@CNT with that of SnO-C and SnO-B. The detailed Li-storage performance of SnO-B is discussed in our previous report [26]. It can be seen that all the samples; SnO-C, SnO-B, SnO-S and SnO@CNT show high initial discharge capacities, 1500, 1510, 1725, 1810 (±10) mA h g⁻¹, respectively. When charged to 0.8 V, they show high first cycle reversible capacities of 660, 575, 635 and 590 (±10) mA h g⁻¹, with first cycle coulombic efficiencies as 44, 38, 37 and 33 %, respectively. The SnO-S showed capacity fading when cycled until 50 cycles and the reversible charge capacity at the end of 50th cycle is 450 (±10) mA h g⁻¹. The capacity fading for SnO-S is 3.7 mA h g⁻¹ per cycle (Table.1). The SnO@CNT showed almost a stable capacity until 50th cycle and the reversible capacity noticed is 500 (±10) mA h g⁻¹. The capacity fading for SnO@CNT is 1.8 mA h g⁻¹ per cycle. It can be seen that both SnO-S and SnO@CNT show better capacity retention compared to that of SnO-C and SnO-B.(Table.1 and Ref. 26). The SnO@CNT shows the best Li-cycling performance among all with least capacity fading. The improved Li- storage performance and better capacity retention is possibly due to the presence of CNT, which provide better electronic conductivity and accommodate the volume change during cycling. At the end of 50th cycle, all the samples showed 96-98 % coulombic efficiency (Fig.6c). The calculated specific energy of SnO-C, SnO-B, SnO-S and SnO-CNT are 330, 288, 318 and 295 (±5) W h/kg, respectively.

Fig. 6b shows the capacity vs. cycle number plots for SnO.CoO-B of different compositions up to 50 cycles at 60 mA g⁻¹ current density. The capacities for different cycles

along with capacity fading and coulombic efficiencies are mentioned in Table.1. It can be seen from Fig.6b that both composition showed almost same discharge and charge capacities until 50th cycles. However, the composition with higher CoO wt.% showed slightly lower capacity as CoO did not contribute to the total capacity in this voltage range. The composition with higher CoO wt.% showed better capacity retention when cycled until 50 cycles and the capacity fading is 1.0 mA h g⁻¹ per cycle against the lower CoO wt.% composition which showed 1.2 mA h g⁻¹ per cycle. This observation is expected as presence of CoO helps to buffer the volume change of SnO during cycling. It can be seen that the better capacity retention was noticed for SnO.CoO-B composite compared to SnO-C, SnO-S and SnO-B. This effect can be explained as the presence of secondary phase (CoO in this study). Hence, the reduction of particle size as well as presence of secondary phase are beneficial for better Li-storage performance and long term cycling. The capacity retention of SnO.CoO-B is little higher compared to SnO@CNT. However, the SnO.CoO-B suffers from low specific capacity. Both the composition show high first discharge capacity of 1395 and 1365 (±10) mA h g⁻¹, whereas the first charge capacities are 460 and 445 (±10) mA h g⁻¹. They show almost a stable cycling performance until 50th cycle. The reversible charge capacities observed at the end of 50th cycles are 400 and 395 ±10) mA h g⁻¹. The SnO.CoO-B shows coulombic efficiency of 96-98% in the range of 5-50th cycle for both the compositions. The calculated specific energy of SnO.CoO-B is 240 (±5) W h/kg, which is lower than SnO-S.

4. Conclusions

We prepared SnO nanoparticles (SnO-S) and SnO.CoO nanocomposites (SnO.CoO-B) as negative electrode materials for lithium ion batteries (LIBs) by chemical route and high energy ball milling approaches, respectively. The structure and morphology are evaluated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. The XRD

shows phase pure formation of SnO-S, whereas the ball milled nanocomposite consists of SnO₂ and Co- metal phases. In both cases, nano-size particles were achieved as confirmed from TEM measurement. The Li- storage performances of SnO-S and SnO.CoO-B are evaluated by galvanostatic cycling and cyclic voltammetry (CV) against Li- metal. Their electrochemical performances are compared to that of commercial micron size SnO (SnO-C) and ball milled SnO (SnO-B). The SnO-S and SnO.CoO-B showed improved cycling performance due to their finite particle size (i.e. nano-size) and presence of secondary phase (CoO). They showed a high reversible charge capacity of 450 and 400 (± 10) mA h g⁻¹, respectively after 50th cycle with capacity fading of 3.7 and 1.2 mA h g⁻¹ per cycle. These values are still higher than that of SnO-C and SnO-B, which show capacity fading of 21.3 and 7.7 mA h g⁻¹ per cycle. Also, addition of carbon nanotubes (CNT) to SnO-S further improved the cycling performance of SnO-S. When cycled at 60 mA g⁻¹, it showed a high reversible capacity of 500 (± 10) mA h g⁻¹ at the end of 50th cycle with capacity fading of 1.8 mA h g⁻¹ per cycle. The coulombic efficiency for all the samples is, 96-98% in the range of 5-50 cycles.

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Table.1. Capacity, coulombic efficiency and capacity fading at different cycle numbers for SnO-C, SnO-B, SnO-S, SnO@CNT and SnO.CoO-B are given.

	SnO-C (mA h g ⁻¹)	SnO-B (mA h g ⁻¹)	SnO-S (mA h g ⁻¹)	SnO@CNT (mA h g ⁻¹)	$\frac{2}{3}$ SnO. $\frac{1}{3}$ CoO-B (mA h g ⁻¹)	$\frac{3}{4}$ SnO. $\frac{1}{4}$ CoO-B (mA h g ⁻¹)
1 st disch.	1500	1510	1725	1810	1365	1395
1 st charge	660	575	635	590	445	460
2 nd disch.	675	600	665	640	460	490
2 nd charge	590	565	630	590	445	465
50 th disch.	190	195	460	515	400	410
(22 cyc.)						
50 th charge	190	190	450	500	395	400
(22 cyc.)						
Capacity fading/ Cycle (mA h g ⁻¹)	21.3	7.7	3.7	1.8	1.0	1.2
	44	38	37	33	33 (1 st cyc.)	33 (1 st cyc.)
	(1 st cyc.)	(1 st cyc.)	(1 st cyc.)	(1 st cyc.)		
Coulombic efficiency; %	96-98 (5-50 cyc.)	96-98 (5- 50 cyc.)	96-98 (5- 50 cyc.)	96-98 (5-50 cyc.)	96-98 (5-50 cyc.)	96-98 (5-50 cyc.)

Figure captions

Fig.1. Powder XRD diffraction patterns: (a) SnO-S nanoparticles prepared at 200 °C, 3 h, Ar; (b) SnO-B (i) and SnO.CoO-B (ii) prepared by high energy ball milling for 18 h in Ar. ($h k l$) values are given.

Fig.2. TEM (a) and HR-TEM (b-d) images of SnO-S. Inset is the SAED pattern of SnO-S. TEM (e) and HR-TEM (f) images of SnO.CoO-B nanocomposite. Scale bars are shown.

Fig.3. Cyclic voltammograms of (a) SnO-S in the voltage window of 0.005-1.0 V and (b) SnO.CoO-B in the voltage window of 0.005-0.8 V at scan rate of 58 V s⁻¹.

Fig.4. Galvanostatic cycling of SnO-S: (a) 1st cycle and (b) 2-50 cycles. SnO@CNT: (c) 1st cycle and (d) 2-50 cycles. Voltage window: 0.005-0.8 V. Current density: 60 mA g⁻¹.

Fig.5. Galvanostatic cycling of SnO.CoO-B: (a) 1st cycle and (b) 2-50 cycles. Differential capacity vs. voltage plots of SnO.CoO-B: (c) 1st cycle and (d) 2nd and 50th cycle. Voltage window: 0.005-0.8 V. Current density: 60 mA g⁻¹.

Fig.6. Capacity vs. cycle number plots : (a) SnO-C, SnO-B, SnO-S and SnO@CNT. (b) $\frac{2}{3}$ SnO. $\frac{1}{3}$ CoO-B and $\frac{3}{4}$ SnO. $\frac{1}{4}$ CoO-B nanocomposites. Coulombic efficiency vs. cycle number plots for (c) SnO-S, SnO-B and SnO@CNT. (d) $\frac{2}{3}$ SnO. $\frac{1}{3}$ CoO-B and $\frac{3}{4}$ SnO. $\frac{1}{4}$ CoO-B nanocomposites.

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