Nano-grained SnO₂/Li₄Ti₅O₁₂ composite hollow fibers via sol-gel/electrospinning as anode material for Li-ion batteries

Anulekha K. Haridas a,b,1, Chandra S. Sharma b,*, Neha Y. Hebalkar a, Tata N. Rao a,**

a Centre for Nanomaterials, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Hyderabad, Telangana, India
b Department of Chemical Engineering, Indian Institute of Technology, Hyderabad, Kandi, Telangana, India

** Corresponding author.
E-mail addresses: cssharma@iith.ac.in (C.S. Sharma), tata@arci.res.in (T.N. Rao).

1 Present address: Department of Chemical and Biomolecular Engineering, Rice University, Houston, Texas, 77005, USA.

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A B S T R A C T
The high capacity of SnO₂ (tin oxide) and high rate capability of Li₄Ti₅O₁₂ (lithium titanate, LTO) were pooled together for engineering a composite Li ion anode material in hollow fiber edifice by sol-gel/electrospinning. The electrospun porous precursor composite hollow fibers (CHFs) were heat treated either in air (SnO₂/LTOA) or argon (SnO₂/LTOAr) atmosphere to control grain size, porosity and presence of Ti³⁺ content. The morphological study performed using Field Emission Scanning Electron Microscopy and Transmission Electron Microscopy revealed smaller grain size (5–10 nm) for SnO₂/LTOAr CHFs. Further, X-Ray Diffraction and X-Ray Photoelectron Spectroscopy studies illustrated a significant variation in the crystallinity and the elemental oxidation states in these CHFs respectively. Brunauer-Emmett-Teller measurements exposed the presence of high surface area and pore volume in SnO₂/LTOAr CHFs. Further, the half-cell galvanostatic charge-discharge performances of SnO₂/LTOAr CHFs at 1 C rate revealed a stable specific capacity of 300 mA h/g for 110 cycles with 90% capacity retention. The stable and high capacity of SnO₂/LTOAr CHFs were corroborated to the presence of smaller grain size, high porosity and conductive Ti³⁺ providing faster lithium ion diffusion when compared to SnO₂/LTOA CHFs. Electrochemical Impedance Spectroscopy study confirmed low impedances in SnO₂/LTOAr CHFs due to low charge transfer and electrolyte resistances. Moreover, Li ion full-cell study performed using LiFePO₄ (LFP) cathode (3 V), delivered a specific capacity of 230 mA h/g at 0.1 C rates. The excellent electrochemical performance of SnO₂/LTOAr CHFs in both half-cell and full-cell modes illustrated the significance of sol-gel/electrospinning in synthesizing high performance Lithium ion batteries in a cost effective and scalable way.

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1. Introduction

Design and synthesis of high performance Li ion battery electrode materials by scalable processes are on high demand as LIBs are being used in various electronic applications and electric vehicles [1,2]. Specific capacity, cell voltage and rate capability are the three major parameters that have to be taken into consideration while engineering an electrode material. The present lithium ion battery electrode materials with high capacities and energy densities such as Sn/SnO₂ and Si/SiO₂ were affected by huge volume expansion during lithium insertion (charging) as a result of the alloying reaction with lithium [3–9]. During cell discharge, de-alloying process causes disintegration of the crystal structure and result in poor contact between electrode material and current collector ensuing rapid capacity fading. Moreover, mechanical disintegration during de-alloying generates fractured metal surfaces. These fractured metal surfaces reacts with electrolyte and lead to loss of active metal from the electrode. Despite of these disadvantages, Sn/SnO₂ is still considered as a significant anode material as they can accommodate 4.4 Li providing a theoretical capacity of 782 mA h/g with maximum volume expansion of 300% [3,10,11].

Several methods were employed to tackle the volume expansion and mechanical disintegration of Sn based electrode materials. In these methods, porosity and minimizing particle size control by nanostructuring are mainly being explored [3,5,10,11]. Meanwhile, nanostructured Sn and SnO₂ in the form of hollow morphologies such as tubes and spheres were attempted by researchers and were
found to be effective in improving the electrochemical performances when compared to the solid nanostructures [12]. However, the capacity fade still remained an unsolved issue as the crystal structure disintegration of Sn/SnO2 cannot be arrested by these designs. In order to address the capacity fade, nanocomposites of these materials were prepared with carbon nanotubes, graphene or mesoporous carbon to create porosity, electrode structure integrity and also for improving electronic conductivity [13–19]. Even though the performances of these Sn based carbon nanocomposites showed excellent capacity values, the consistency in composite preparation, cost effective scaling up methods, as well as varying electrochemical performances are serious issues in a commercialization point of view. Hence research endeavors like in situ synthesis of SnO2 composites with other metal oxides such as TiO2 (SnO2/TiO2) [20–22] and LTO (SnO2/LTO) [23–25] were explored. The presence of second oxide phase in these composite systems minimized the volume expansion and pulverization of Sn by forming smaller sized particles during fabrication of the composite [20–29]. However, these composite structures failed to provide high rate capability and cycle stability due to their low conductivity as well as low porosity caused diffusion limitation. Thus an ideal SnO2 based anode that is expected to minimize the growth of Sn particles can be a highly conductive and porous nanocomposite comprising of SnO2 and another oxide.

In order to address diffusion limitation and the low conductivity in the above mentioned SnO2/oxyde composites, we have designed a new anode material in the form of SnO2/LTO composite hollow fibers (CHFs) with considerable Ti3+ in the lattice. This unique structure with high porosity can ease Li ion diffusion in the electrode. As the cycle stability and high rate capability of LTO is well known due to its zero strain nature (~0.2% volume expansion) during lithium ion insertion and desertion [30–35], an improved structural integrity is expected for the SnO2/LTO composite anode. LTO is also a high voltage anode material (1.55 V versus Li) that provides (Scheme 1) for illustrating the synthesis of hollow fibers in air and argon atmospheres respectively. A schematic is provided in our earlier publication [32] using TIP and lithium acetate di hydrate in Li: Ti ratio 4: 5. Then the SnO2 sol and LTO sol were mixed in 1:1 ratio by stirring for 1 h, and electrospun into SnO2/LTO precursor CHF.

As a control study, SnO2/PEO precursor fibers were also prepared by electrospinning from a blend of SnO2 sol and 20 wt% PEO solutions (in water). E-spin Nano machine, India was used for electrospinning process using 10 ml syringes fitted with 21 gauge needles. A voltage of 25 kV and 10 cm distance between the electrodes were maintained during electrospinning process and an aluminum foil was used for collecting the electrospun precursor fibers. A part of these SnO2/LTO precursor CHFs were then calcined in air at various temperatures 550, 650 and 750 °C for 1 h to obtain SnO2/LTOa CHFs. Another part of SnO2/LTO precursor CHFs were annealed in argon atmosphere at 550 and 650 °C for 4 h to obtain SnO2/LTOb CHFs. Similarly, bare SnO2 fibers and SnO2/C fibers were prepared by heat treating the electrospun SnO2/PEO precursor fibers in air and argon atmosphere respectively. A schematic is provided (Scheme 1) for illustrating the synthesis of hollow fibers in air and argon atmospheres and were named hereafter as SnO2/LTOa and SnO2/LTOb respectively.

2.3. Material characterization

Morphology of SnO2/LTOa and SnO2/LTOb CHFs was analyzed using Field Emission Scanning Electron Microscopy (FESEM, Hitachi model- S4300SE/N). The hollow nature and particle size in the fibers were further studied by Transmission electron microscopy (TEM, Tecnai G2 TF20 TWIN) at an operating voltage of 200 kV. X-Ray diffraction (XRD, Bruker D8 with Cu Kα radiation) was used for understanding the crystallinity and phase formation in the fibers from 10 to 80° angle. The diffraction patterns were then analyzed using Match software with JCPDS data cards for confirming the phase formation. The elemental composition and their oxidation states in the CHFs were also studied using X-ray Photo electron spectroscopy (XPS, Omicron with Al Kα radiation). The surface area, pore size and pore volume of the samples, were studied using surface area and porosity analyzer (Micrometrics ASAP 2020) using BET and BJH method.

2.4. Electrode preparation and electrochemical characterizations

Electrodes of SnO2, SnO2/C fibers and SnO2/LTOa and SnO2/LTob CHF were made by preparing slurries of the respective fibers (80 wt %) with conductive carbon (10 wt %) and PVDF (10 wt %) in N-methyl pyrrolidone. The prepared slurries were coated on battery grade Cu foil obtained from MTI Corporation, United States and was dried in vacuum for 18 h. Circular discs of 12 mm diameter were cut from the dried Cu foils and were assembled into coin cells inside glove box in argon atmosphere. Whatman micro glass fibers were
used as separator and Li foil was used as the counter electrode. 1 M LiPF₆ dissolved in ethyl carbonate (EC) and dimethyl carbonate (DMC) was used as electrolyte (EC: DMC = 1:1). Electrochemical half-cell performance of bare SnO₂ fibers, SnO₂/C fibers, SnO₂/LTOA CHFs and SnO₂/LTOAr CHFs were studied using Arbin Instruments from 0.02 V to 1.5 V at various charging rates. Cyclic voltammetry studies were carried out at a scan rate of 0.02 mV/s for 6 cycles. Further, electrochemical impedance measurements were conducted at frequency range of 0.01–100 MHz using electrochemical impedance analyzer Solartron, at amplitude of 10 mV. For demonstrating the working of SnO₂/LTO CHFs in a complete Li ion cell, SnO₂/LTO CHFs were blended and electrospun into SnO₂/PEO fibers. SEM image of electrospun SnO₂/PEO precursor fibers (control study) was observed with fiber diameters in 700 nm – 1 μm range (Fig. S3A). Fig. 1A and B shows the FESEM images of as-spun SnO₂/LTO precursor hollow fibers (A and B), air treated SnO₂/LTOa CHFs (C) and argon treated SnO₂/LTOar CHFs (D). XRD pattern of SnO₂/LTOa CHFs (750 °C) and SnO₂/LTOar CHFs (650 °C) are shown in E.

### 3. Results and discussion

#### 3.1. Formation of SnO₂/LTO CHFs: morphology and phase analysis

SnO₂ and LTO sols were mixed in 1:1 M ratio and aged for various time intervals to obtain SnO₂/LTO precursor spinning solutions. Prior to electrospinning, the viscosities of spinning solutions were measured as 14 ± 2 mPa s, 40 ± 5 mPa s and 70 ± 10 mPa s respectively for 6 h, 48 h and 7 days of ageing. Electrospun sols after 6 h, 48 h and 7 days of aging yielded particles, dimpled spheres and hollow fibers respectively. A detailed description about formation of various structures on electrospinning is provided in the supplementary information (Fig. S1 and S2). Meanwhile, SnO₂ sol and PEO solution (in 1:1 vol ratio) were mixed and electrospun into SnO₂/PEO fibers. SEM image of electrospun SnO₂/PEO precursor fibers (control study) was observed with fiber diameters in 700 nm – 1 μm range (Fig. S3A).

Here, the formation of fiber morphology during electrospinning was correlated to the sol ageing period which in turn was related to the viscosity of the spinning solution. As the gelation time was increased, viscosity of spinning solution was also observed as increasing within seven days yielding fiber morphology. Similar results were observed in our previous studies with LTO sol which resulted in particles, donut structures and rod shaped structures as a function of solution viscosity [32]. The formation of porous hollow fiber morphology can be attributed to the differences in volatilities of solvent mixtures (ethanol and isopropanol) in the spinning solution [39]. During electrospinning process, SnO₂/LTO precursor materials in the spinning fiber are driven in the radial direction. The more volatile solvent ethanol evaporates faster creating a concentration difference of ethanol and isopropanol in the spinning fiber. As the volatility of isopropanol is also in the similar range of ethanol, soon after the evaporation of later,
isopropanol also escapes from the structure creating porous hollow fiber morphology.

In order to obtain SnO$_2$ and LTO phases in the hollow fibers, the precursor CHFs were calcined in air and argon atmospheres at various temperatures. FESEM images of SnO$_2$/LTO$_{A}$ and SnO$_2$/LTO$_{Ar}$ CHFs obtained after calcination in air ($750 \degree$C) and argon ($650 \degree$C) atmospheres respectively were displayed in Fig. 1C and D. The air heat treated SnO$_2$/LTO$_{A}$ hollow fibers at $750 \degree$C were perceived with diameters in the range of 1–2 μm. Meanwhile, electrospun SnO$_2$/PEO fibers were heat treated in air and argon atmospheres to obtain SnO$_2$ fibers and SnO$_2$/C fibers respectively. SEM images of SnO$_2$ fibers and SnO$_2$/C fibers were provided in Fig. S3B and S3C respectively.

As the temperature of calcination was increased from 550 to $750 \degree$C, crystallinity in the SnO$_2$/LTO$_{A}$ CHFs was perceived as increasing, as shown by XRD pattern in Fig. S4A. The presence of both SnO$_2$ (cassiterite) and LTO (spinel) phases in the CHFs were confirmed by matching with JCPDS data cards 41-1445, (space group P42/mnm) and 04-016-2284 (space group Fd3m) respectively. The planes (110), (101), (200), (211) and (301) are matched with cassiterite phase of SnO$_2$ whereas (111), (311), (400), (333) and (440) are matched with spinel phase of LTO. XRD pattern of bare SnO$_2$ fibers obtained by heat treating electrospun SnO$_2$/PEO fibers

**Fig. 2.** TEM images of SnO$_2$/LTO$_{A}$CHFs (A1, B1) and SnO$_2$/LTO$_{Ar}$ CHFs (A2, B2) showing the hollow nature and the presence of small grains.

**Fig. 3.** A in the Fig. indicates the XPS surface spectrum of SnO$_2$/LTO$_{A}$ and SnO$_2$/LTO$_{Ar}$ CHFs. Sn, Ti, O, Li and C de-convoluted peaks in the CHFs are depicted in B, C, D, E and F of the figure.
at 750 °C are also provided in Fig. S4A. Similarly, argon heat treatment was conducted from 550 to 650 °C for 4 h. Here, the argon heat treatments were limited up to 650 °C due to the chance of losing Sn at higher temperatures. XRD patterns of the argon treated samples at 550 and 650 °C are shown in Fig. S4B. XRD pattern of SnO₂/C fibers obtained by heat treating electrospun SnO₂/PEO fibers at 650 °C in argon are also provided in Fig. S3B. SnO₂/LTOAr hollow fibers at 650 °C were observed with broad peaks of SnO₂ and LTO when compared to the air heat treated SnO₂/LTOAr CHFs at the same temperatures. XRD pattern of SnO₂/LTOAr (750 °C in air) and SnO₂/LTOAr (650 °C in argon) were provided in Fig. 1E and were chosen for further characterizations and electrochemical studies as they were of higher crystallinity in the respective atmospheric heat treatments.

TEM analysis of the SnO₂/LTOAr and SnO₂/LTOAr CHFs were given in Fig. 2A1 and 2A2 respectively. A bright interior and dark exterior contrast difference was observed in both CHFs confirming the hollow morphology.

Further, the high magnification TEM images (Fig. 2B1 and B2) revealed porous nature of CHFs with the presence of small sized grains. The grain size of SnO₂/LTOAr (Fig. 2B1) was about 10–30 nm, whereas SnO₂/LTOAr was observed with grains ranging from 5 to 15 nm in diameter with a small fraction of bigger grains (Fig. 2B2). The smaller grain sizes observed in SnO₂/LTOAr can be attributed to the controlled heat treatment which reduced the grain growth in the absence of oxygen that would rather happen in the air atmosphere. The selected area diffraction (SAED) pattern of SnO₂/LTOAr CHFs and SnO₂/LTOAr CHFs were observed as dark and bright circular bands. The bright diffraction pattern in SnO₂/LTOAr CHFs indicated their highly crystalline nature, whereas the diffused pattern in SnO₂/LTOAr CHFs indicated the presence of smaller crystallites in the amorphous matrix (Fig. S5 A and B).

### 3.2. XPS study of SnO₂/LTO CHFs

In order to understand the oxidation states of Sn and Ti in SnO₂/LTOAr and SnO₂/LTOAr CHFs XPS study was performed in the binding energy range of 0–800 eV. The surface spectra of CHFs (Fig. 3A) revealed the presence of tin, oxygen, titanium and carbon. The composition of both CHFs are represented in Table S1.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Hollow fibers</th>
<th>BET surface area (m²/g)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnO₂/LTOAr</td>
<td>102.40</td>
<td>4.64</td>
<td>0.11</td>
</tr>
<tr>
<td>2</td>
<td>SnO₂/LTOA</td>
<td>12.55</td>
<td>28.40</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Fig. 4. Nitrogen adsorption-desorption isotherms (A) and pore size distribution (B) of SnO₂/LTOAr and SnO₂/LTOA CHFs.

Fig. 5. Cyclic Voltammetry studies of SnO₂/LTOA (A) and SnO₂/LTOAr CHFs (B) at a scan rate of 0.02 mV/s.
elemental ratio of Sn and Ti in SnO2/LTOA and SnO2/LTOAr hollow fibers were observed as 0.8:1 and 0.6:1 respectively.

The Sn 3d5/2 peaks in SnO2/LTOA and SnO2/LTOAr hollow fibers were observed at binding energy 486.6 eV and 486.75 eV respectively (Fig. 3B). This indicated the presence of Sn4+ in the CHFs with Sn bonded to oxygen as in SnO2 [40]. Further, the Ti 2p3/2 peak at 458.7 eV in SnO2/LTOA CHFs was co-related to the presence of Ti4+ which had Ti bound to O as in LTO [36,37] (Ti 2p3/2, Ti 2p1/2 = 458.74, 464.56 eV). Whereas the Ti 2p3/2 peak in SnO2/LTOAr hollow fibers was observed at 456.1 eV which was seen shifted to lower binding energy by 2.6 eV indicating the presence of Ti3+ oxidation state (Fig. 3C).

The de-convolution of O 1s peak (Fig. 3D) in SnO2/LTOA CHFs have shown two peaks at 529.52 eV and 530.16 eV pertaining to O-Ti and O-Sn bonds respectively as observed in LTO and SnO2 [40–42]. Lithium was detected in both the CHFs at 55 eV that matched the Li+ oxidation state (Fig. 3E). The presence of carbon was detected in both samples, relating the peaks at 284.6 and 285 eV to C-C and C=C respectively [43,44]. SnO2/LTOA CHFs were observed with peaks having higher intensity and slight binding energy shift towards lower value when (Fig. 3F) compared to SnO2/LTOAr CHFs with peaks having higher intensity and slight binding energy shift towards lower value when (Fig. 3F) compared to SnO2/LTOAr CHFs. Additionally, the presence of C=C–O was detected in SnO2/LTOA hollow fibers at 258.91 eV [43]. In summary, SnO2/LTOA CHFs were confirmed with the presence of both SnO2 and LTO phases, whereas a lower binding energy in Ti–O bond of SnO2/LTOAr CHFs confirms a valance reduction of Ti to +3. The presence of Ti3+ in SnO2/LTOA CHFs was advantageous as it can contribute to high electronic conductivity and faster Li ion intercalation. Thus, the presence of SnO2 and LTO in both the CHFs was confirmed.

3.3. Surface area and porosity of SnO2/LTO CHFs

Surface area measurements were carried out for understanding the porosity, pore size and pore volume in the CHFs and the results were summarized in Table 1. Nitrogen adsorption–desorption isotherms of SnO2/LTOA and SnO2/LTOAr CHFs in Fig. 4A represent type IV isotherms with type III [45] and type H2 [10,14,46] hysteresis loops respectively, that evidenced the mesoporous nature.

In SnO2/LTOA CHFs closure of isotherm loop around 0.4 relative pressures (P/P0) confirmed the presence of pore less than 10 nm in size [47]. SnO2/LTOA CHFs showed a higher hysteresis than SnO2/LTOA CHFs pertaining to a more porous nature than the later (Fig. 4A). The BET surface areas for SnO2/LTOA and SnO2/LTOAr CHFs were measured as 12.55 m2/g and 102.40 m2/g respectively. On analyzing the pore size distribution by BJH method, SnO2/LTOA CHFs were perceived with more uniform sized pores than in SnO2/LTOAr CHFs (Fig. 4B). The BJH pore size and pore volumes of SnO2/LTOA and SnO2/LTOAr CHFs were measured as 28.8, 4.64 nm and 0.09, 0.11 cm3/g respectively.

The BET surface area and BJH pore volume results were in accordance with the TEM images (Fig. 2B1 and B2) that confirmed the presence of small sized grains in SnO2/LTOA CHFs providing higher surface area and porosity when compared with SnO2/LTOAr CHFs.

In the nutshell high surface area and porosity observed in both CHFs can aid in reducing the lithium ion diffusion length and also ease in accommodating the huge volume expansion during Li insertion. To validate this, electrochemical studies were performed and were discussed in following sessions.

\[
\text{Li}_3\text{Ti}_5\text{O}_{12} + 4.5\text{Li}^+ + 4.5e^- \rightarrow \text{Li}_{13.5}\text{Ti}_5\text{O}_{12}
\]

Scheme 2.

3.4. Cyclic voltammetry studies

Cyclic voltammetry studies were conducted for the CHFs in the voltage range of 0.05–2 V at a scan rate of 0.02 mV/s (Fig. 5). During the initial discharge cycle which started from the cell open circuit voltage (OCV) 2.5 V, both types of CHFs have shown reduction peaks at 1.54, 1.46, 1.02, 0.5, 0.3 and 0.2 V respectively. First and last reduction (cathodic) peaks in Fig. 5 was due to the respective reduction of Ti4+ to Ti3+ and formation of SnLi alloy during Li intercalation [27,48,49]. The remaining irreversible cathodic peaks are due to the Solid Electrolyte Interphase (SEI) layer formed by the decomposition of electrolyte to Li2O and conversion of SnO2 to Sn. The oxidation peaks at 0.5 V represented the Sn (de-alloying) during cell discharge. The oxidation peaks at 1.3 and 1.59 V were accredited to the formation of SnO2 and oxidation of Ti4+ to Ti3+ respectively. The second and third cycles showed reduction peaks at 1.54 V, 0.2 V and oxidation peaks at 1.59 V, 0.5 V which were for Ti redox couple and Sn alloying/de-alloying couples respectively, attributing the reversible nature of both the CHF electrodes.

The mechanism of Li cycling with both CHF electrodes can be explained as combination mechanisms of conversion and intercalation in the first cell discharge as shown in the following Schemes 2–4.

Later the alloy/de-alloy mechanism of Sn dominates and contributed to the reversible capacity of the electrodes (in the voltage range 0.05–2 V) as follows [9,50] (see Scheme 5).

3.5. Galvanostatic charge–discharge studies

In order to compare the charge/discharge stability performance, SnO2 bare fibers, SnO2/C, SnO2/LTOA CHFs and SnO2/LTOAr CHFs were cycled at 0.1 C for 11 cycles from 0.05 to 1.5 V respectively (Fig. 5E). The charge-discharge profiles of the four fiber samples have shown high capacities in the first cycle. For SnO2 fibers a clear plateau was observed at 0.8–1.2 V indicating the reduction of Sn4+ to Sn3+ and formation of Li2O [51]. The reduction reactions of SnO2 are given in Schemes 3 and 4. The same phenomenon was observed with SnO2/C, SnO2/LTOA and SnO2/LTOAr CHFs respectively (Fig. S6B and D).

SnO2 bare fibers have experienced drastic capacity fading in the first 10 charge–discharge cycles at 0.1 C rate (Fig. S6A). This was due to their large volume expansion and structure disintegration experienced while alloying and de-alloying with lithium. For SnO2/C fibers a slight improvement in cycle stability was perceived whereas, SnO2/LTOA and SnO2/LTOAr CHFs showed higher cyclic stability with less capacity fading (Fig. S6B and D).

For a better comparative study, the columbic efficiency of the four fiber samples was provided in Fig. S7. The bare SnO2 fibers and SnO2/C fibers were detected with an initial columbic efficiency of 27.9% and 28.4% respectively. Meanwhile, the first cycle could
efficiency SnO$_2$/LTO CHFs and SnO$_2$/LTO$_{A}$ CHFs were observed as 36% and 46% respectively. As the charge-discharge proceeded to 11 cycles, the coulombic efficiency values in all fiber samples were observed as increasing. The 11th cycle coulombic efficiency for the SnO$_2$ and SnO$_2$/C fibers were perceived as 83% and 91% respectively. At same time, at the end of 11th cycle, 97, 93% coulombic efficiency was observed for SnO$_2$/LTO$_{A}$ and SnO$_2$/LTO$_{Ar}$ CHFs respectively. The electrochemical performance in the four electrodes can be represented in the following order:

SnO$_2$ fibers > SnO$_2$/C fibers > SnO$_2$/LTO$_{A}$ CHFs > SnO$_2$/LTO$_{Ar}$ CHFs

The improved cyclic performance of both CHFs can be ascribed to their porous and hollow architecture with smaller grain sizes and better structural integrity due to the presence of electrochemically stable LTO grains (zero crystal stain) in the neighbourhood of SnO$_2$ particles.

For further understanding the high rate capability of the SnO$_2$/LTO$_{A}$ and SnO$_2$/LTO$_{Ar}$ CHF electrodes, charge-discharge studies were conducted at higher C rates in the order of 0.3, 0.5, 0.8, 1, 2 and 5 C (Fig. 6). When compared with SnO$_2$/LTO$_{A}$ CHF, SnO$_2$/LTO$_{Ar}$ CHF were perceived with greater cycle stability and lower capacity fading as the charging rates of the cells were increased (Fig. 6A and C). For instance at charging rates of 0.3, 0.5, 0.8, 1, 2 and 5 C, SnO$_2$/LTO$_{A}$ CHFs have retained discharge capacities of 540, 452, 417, 362, 320, 250 and 145 mAh/g respectively whereas, SnO$_2$/LTO$_{Ar}$ CHFs were observed with 435, 390, 363, 350, 330, 320 and 270 mAh/g. For a better comparative study, charge-discharge capacities of both CHFs at various C rates have been tabulated in Table 2.

At charging rates higher than 1 C SnO$_2$/LTO$_{A}$ CHFs were observed with a slight capacity fading in 10 cycles whereas, SnO$_2$/LTO$_{Ar}$ CHF delivered 100% capacity retention. After the sequential rate performance study up to 5 C and when charged back to 1 C, SnO$_2$/LTO$_{Ar}$ CHFs could retain the same capacity (330 mAh/g), however SnO$_2$/LTO$_{A}$ fibers were observed with a capacity loss of 7% from the initial value.

Further, when the charge-discharge studies was continued at 1 C rate for 110 cycles, SnO$_2$/LTO$_{A}$ CHFs were perceived with significant capacity fading from 300 to 150 mAh/g (Fig. 6B) providing only 50% capacity retention. Whereas, SnO$_2$/LTO$_{Ar}$ CHFs were observed with a very little capacity fading (from 330 to 310 mAh/g) having almost 90% capacity retention (Fig. 6D).

Moreover a comparative study of the battery performances of SnO$_2$ LTO based electrodes, with the available literature is provided in Table 3. SnO$_2$/LTO CHFs prepared in our study was observed as superior to the reported literature in terms of specific capacity values, Cycle stability as well as percentage capacity retention. Also, among the two CHFs synthesised in our study, the reason for superior rate capability and cycle stability for SnO$_2$/LTO$_{Ar}$ CHFs can be as due to their smaller particle size, higher surface area and larger pore volume that enabled a lower lithium ion diffusion length than the latter. Moreover, the presence of Ti$^{3+}$ in SnO$_2$/LTO$_{Ar}$ CHFs might have provided higher electronic and ionic conduction enabling easy and fast alloying of Li ions when compared with the latter [14,15,17]. For validating the above sentence electrochemical impedance studies were conducted for SnO$_2$/LTO$_{A}$ and SnO$_2$/LTO$_{Ar}$ CHFs.

3.6. Electrochemical impedance studies

Nyquist plot were recorded for SnO$_2$/LTO$_{A}$ and SnO$_2$/LTO$_{Ar}$ CHFs after 10 (Fig. 7A) and 110 (Fig. 7B) charge-discharge cycles. The presence of electrolyte resistance (Re), surface layer resistance (Rs) and charge transfer resistance (Rct) were detected in the Nyquist plots representing two semicircles indicating two time constants. Electrochemical impedance circuit fit results of both types of composite fibers were summarized in Table 4. The semicircle that appeared in the higher frequency region was due to the resistance of surface layer formed on the electrode and the one in the lower

![Fig. 6. Galvanostatic charge discharge studies of SnO$_2$/LTO$_{A}$ and SnO$_2$/LTO$_{Ar}$ CHF at varying C rates (A and C). 110 cycles of charge discharge stability studies of SnO$_2$/LTO$_{A}$ (B) and SnO$_2$/LTO$_{Ar}$ CHFs (D) at 1 C rate.](image-url)
The frequency region was ascribed to the charge transfer resistance of the electrode material.

An increase in the Re electrolyte resistance value was observed after 110 cycles of charge discharge (when compared with the 10 cycle Re) in both the CHFs demonstrating the building up of SEI layer. SnO2/LTOAr CHFs was speculated with formation of low SEI layer according to the low Re values. Moreover, Rct in both the CHFs have witnessed lower value after 110 cycles representing fast Li alloying/de-alloying. This was described as follows: During long cycling, SEI provided the conductive paths for lithium ions by reducing the overall cell resistance. Among the CHFs, SnO2/LTOAr evidenced superior performance with lower Re (8.29 Ω) and Rsl (113 Ω) in comparison to SnO2/LTOA after 110 cycles. Further SnO2/LTOAr CHFs was detected with Rct values almost three times lower (306 Ω) than SnO2/LTOA CHFs (987 Ω). The lower Rct observed with SnO2/LTOAr CHFs was accredited to the presence of conductive Ti3+, smaller grain sizes as well as high surface areas than SnO2/LTOA CHFs, which were already confirmed by the XPS, TEM images and BET surface area measurements. Similarly the lower Rsl in the SnO2/LTOAr CHFs was ascribed to the lower growth of surface layer after each charge-discharge cycle.

3.7. Complete Li-ion cell (full cell) using SnO2/LTOA CHF anode and LFP cathode

For understanding the working of CHF in a full Li ion cell, the better performed SnO2/LTOA CHF anode in half cell was chosen for full cell studies. SnO2/LTOA CHF anode was assembled with commercially available LiFePO4 (LFP) cathode. The anode to cathode weight ratio was maintained 1:3 in order to compensate for the Li loss in SEI. Fig. 8A illustrates the GCD profile for LFP/Li, SnO2/LTOA CHFs/Li and SnO2/LTOA CHFs -LFP cells charged-discharged at 0.1 C rates. LFP half-cell was observed with a voltage of 3.5 V and specific capacity 161 mAh/g whereas SnO2/LTOA CHF half-cell was perceived with a voltage of 0.5 V and 600 mAh/g specific capacity. The SnO2/LTOA CHFs –LFP full cell has delivered a voltage of 3 V and specific capacity 230 mAh/g. In comparison with the individual

Table 2
Discharge capacities of SnO2/LTO CHFs (after first 10 cycles) at various C rates.

<table>
<thead>
<tr>
<th>Composite hollow fiber samples</th>
<th>1st and 10th cycle specific capacity (mAh/g) of samples at various C rates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1 C</td>
</tr>
<tr>
<td></td>
<td>1st</td>
</tr>
<tr>
<td>SnO2/LTOA</td>
<td>1400</td>
</tr>
<tr>
<td>SnO2/LTOAr</td>
<td>1475</td>
</tr>
</tbody>
</table>

Table 3
A competitive study on the battery performance of CHFs with SnO2-LTO electrodes from literature.

<table>
<thead>
<tr>
<th>[Ref]</th>
<th>Type of composite electrode, synthesis method</th>
<th>IC (mAh/g)</th>
<th>Long term cycling studies</th>
<th>CR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[23]</td>
<td>Spray drying (hollow spheres)</td>
<td>530–700</td>
<td>350</td>
<td>170 mA g⁻¹</td>
</tr>
<tr>
<td>[24]</td>
<td>LTO coated hollow SnO2 particles</td>
<td>–</td>
<td>439</td>
<td>1000 mA g⁻¹</td>
</tr>
<tr>
<td>[25]</td>
<td>Combustion</td>
<td>300–442</td>
<td>100–150</td>
<td>100 mA g⁻¹</td>
</tr>
<tr>
<td>[26]</td>
<td>SnO2 coated LTO powders</td>
<td>476</td>
<td>276</td>
<td>0.5 mA cm⁻¹</td>
</tr>
<tr>
<td>[27]</td>
<td>Sol-gel (powders)</td>
<td>688</td>
<td>642</td>
<td>0.2 C</td>
</tr>
<tr>
<td>[28]</td>
<td>Solution precipitation (powders)</td>
<td>600–700</td>
<td>189</td>
<td>0.5 mA cm⁻¹</td>
</tr>
<tr>
<td>[29]</td>
<td>Spray pyrolysis (powders)</td>
<td>380–550</td>
<td>271–312</td>
<td>700 mA g⁻¹</td>
</tr>
<tr>
<td>Our work</td>
<td>Sol-gel/electrospinning (Hollow fibers)</td>
<td>430–540</td>
<td>150–310</td>
<td>1 C–780 mA g⁻¹</td>
</tr>
</tbody>
</table>

Table 4
Summary of Electrochemical impedance results.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Hollow fiber samples</th>
<th>R_e (Ω)</th>
<th>R_i (Ω)</th>
<th>R_sl (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnO2/LTOA CHFs (10 cycles)</td>
<td>8.09</td>
<td>5.93</td>
<td>8.09</td>
</tr>
<tr>
<td>2</td>
<td>SnO2/LTOA CHFs (110 cycles)</td>
<td>14.73</td>
<td>121</td>
<td>987</td>
</tr>
<tr>
<td>3</td>
<td>SnO2/LTOA CHFs (10 cycles)</td>
<td>9.31</td>
<td>10154</td>
<td>44654</td>
</tr>
<tr>
<td>4</td>
<td>SnO2/LTOA CHFs (10 cycles)</td>
<td>11.29</td>
<td>113.8</td>
<td>309.3</td>
</tr>
</tbody>
</table>

SnO2/LTOAr CHFs was accredited to the presence of conductive Ti3+, smaller grain sizes as well as high surface areas than SnO2/LTOA CHFs, which were already confirmed by the XPS, TEM images and BET surface area measurements. Similarly the lower Rsl in the SnO2/LTOAr CHFs was ascribed to the lower growth of surface layer after each charge-discharge cycle.

Fig. 7. Nyquist plots showing electrochemical impedance studies of SnO2/LTOA and SnO2/LTOAr CHF electrodes after 10 cycles (A) and 110 cycles (B) of charge-discharge studies.
half-cells, the SnO2/LTOA CHFs –LFP full cell possesses high energy density as the voltage and capacity delivered are in the higher range. The full cell was charged-discharged for 20 cycles to understand the capacity stability. GCD profile of SnO2/LTOA CHFs –LFP full cell at 1st and 20th cycles was shown Fig. 8B. Even though the first cycle of full cell delivered a charge capacity of 550 mAh/g discharge capacity were about 200 mAh/g correlating to a low coulombic efficiency. On proceeding further cycling, the coulombic efficiency of the full cell was observed as increasing. The 20th cycle discharge capacity was observed 230 mAh/g. The cycle stability and coulombic efficiency of SnO2/LTOAr CHFs –LFP full cell for 20 cycles are given in Fig. 9. An increase in the discharge capacity was observed with the full cell from 1st to 20th cycle. The percentage increase in discharge capacity in 20 cycles can be calculated as 15%. Moreover, an increase in coulombic efficiency of full cell was observed (92%) at the end of 20th cycle.

In graphite –LFP full cell that can deliver 3 V and ideally a capacity of 372 mAh/g w. r. t the mass of anode, an energy density of 1116 Wh/kg can be achieved. By considering the reduction factor of 1/3 for the weight of current collector, electrolyte and aluminum case [52] a practical energy density of 372 Wh/kg can be obtained. Further by considering an additional specific capacity due to weight reduction in high capacity SnO2/LTOAr CHF anode which can offer ~600 mAh/g at 0.1 C in half cell (graphite 372 mAh/g), the SnO2/ LTOAr CHF –LFP full cell can account for an energy density higher than 372 Wh/kg. Hence SnO2/LTO CHFs can be considered as a contender for high capacity anodes similar to Sn and Si for use in high power LIBs.

4. Conclusions

Sol-gel/electrospinning route was selected for fabricating SnO2/ LTOA and SnO2/LTOAr CHF due to its cost effectiveness, ease and reproducibility. The presence of LTO in these CHF has aided in controlling the grain growth of SnO2 during heat treatment, creating nano-sized grains. The FESEM and TEM images of CHFs confirmed their hollow nature with grain sizes 30 nm and 5–20 nm for SnO2/LTOA and SnO2/LTOAr CHFs respectively. XPS studies
revealed the presence of SnO2 and LTO in both the CHFs with a slight reduction in oxidation state for Ti (TiIV) in SnO2/LTOAr CHFs indicating more electronic conduction. Both the CHFs were observed with high rate capability and cycle stability in comparison with the electrosprun bare SnO2 and SnO2/C fibers. Moreover, the porous and hollow nature of fibers has alsoabetted in controlling the volume expansion and pulverization in SnO2 during alloying-de-alloying reactions, and exhibited high rate performances. Further, due to the presence of conductive TiIV, SnO2/LTOAr CHFs provided excellent rate capability in comparison with SnO2/LTOAr CHFs with 90% capacity retention after 110 cycles of charge-discharge. Moreover, low resistances were observed for the same when compare with SnO2/LTOAr CHF in the electrochemical impedance measurements. On attempting the full cell study of de-alloying reactions, and exhibited high rate performances. TNR and AKH acknowledge DST Nanomission, India for financial support. Authors acknowledge Dr Shanti V. Nair and Dr Sajini Seekum of Amrita centre for Nanosciences, Cochin, India in TEM imaging. We also extend our sincere thanks to Mrs A. Jyothirmayi, ARCI, Hyderabad for Impedance measurements.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.mtener.2017.01.002.

References


