Supporting information

Improved electrochemical performance of SnO$_2$ - mesoporous carbon hybrid as a negative electrode for lithium ion battery applications

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A unified view of SnO$_2$ nanoparticle location in mesoporous carbon (CMK-5)

Fig. S1 A unified view of different possible SnO$_2$ nanoparticle location in mesoporous carbon (CMK-5) particles, based on reports in the literature.$^4$-$^23$ SnO$_2$ formation (a) both inside and on the outer surface of mesopores, present within a CMK-5 particle; (b) on both these surfaces, and in addition, also as isolated SnO$_2$ nanoparticles; (c) only on the outer surface of mesopores, present within a CMK-5 particle (as developed in the present work).

Among SnO$_2$-CMK family of electrodes reported so far,$^4$,$^20$-$^23$ different synthesis approaches have led to the formation of SnO$_2$ nanoparticles in different regions of the CMK particles. In a recent report,$^20$ surface of CMK family is modified to allow the tin precursors inside the pores of mesoporous carbon, which leads to SnO$_2$ nanoparticles inside the pores during heating at high temperature under inert atmosphere. As a result, SnO$_2$ nanoparticle
formation occurs on the both inside and outer surface of mesopores, present within CMK-5 (Fig. S1a).

In other reports, \(^{21-23}\) tin precursor is mixed with preformed CMK particles during the synthesis process of SnO\(_2\)-CMK hybrids. This synthesis protocol may lead to allow the tin precursor to diffuse inside and outer surface of the mesopores present in the CMK-5 or between the carbon rods in CMK-3. In addition, there is a possibility for aggregation of SnO\(_2\) nanoparticles in the bulk state. (Fig. S1b).

The present work focuses on the formation of SnO\(_2\) nanoparticles on the outer surface of mesopores, present within CMK-5. (Fig. S1c). SnO\(_2\) nanoparticles present on outer surface of mesopores will utilize the empty space created (after removal of SBA-15 by HF solution) in the CMK-5 particle for volume expansion during charging-discharging cycles. This strategy used in this material design would be a good platform to explore better electrochemical performance for the SnO\(_2\)-CMK-5 family, as well as other metal/metal oxide nanoparticle-ordered porous material hybrid.

**Percentage removal of SBA-15 and SnO\(_2\) by HF solution**

Aqueous HF solution (20% by vol.) is capable of removing SBA-15 as well as SnO\(_2\). Three samples (only SnO\(_2\) nanoparticles, carbon coated SBA-15 particles and carbon coated SnO\(_2\)-SBA-15 particles) were chosen for finding the percentage of SnO\(_2\) and SBA-15 removal during leaching process. First, carbon coated SBA-15 particles were stirred with HF for 30 min. After 30 min, there was no silicon (Si) present in the treated sample (confirmed by SEM-EDX). From this analysis, it is clear that 100 wt. % SBA-15 is removed within 30 min from carbon coated SBA-15 sample. Similarly, the percentage of weight loss (by
gravimetry after 30 min) of only SnO\textsubscript{2} nanoparticle and of SnO\textsubscript{2} particle from carbon coated SnO\textsubscript{2}-SBA-15 is 4.7 wt\% and 1.2 wt. \%, respectively. Therefore, even though the SnO\textsubscript{2}-CMK-5 hybrid sample contains nanostructured SnO\textsubscript{2}, the percentage removal of SnO\textsubscript{2} is very less in comparison to silica in the carbon coated SBA-15.

**Thermogravimetric analysis of SnO\textsubscript{2}-CMK-5**

![Thermogravimetric analysis profile for SnO\textsubscript{2}-CMK-5](image)

**Fig. S2** Thermogravimetric analysis (TGA) profile for SnO\textsubscript{2}-CMK-5.

Thermogravimetric analysis (TGA), carried out at a heating rate of 10 K min\textsuperscript{-1}, in the presence of air, was used to calculate the percentage of SnO\textsubscript{2} in SnO\textsubscript{2}-CMK-5 sample. Before TGA analysis, there will be some amount of physically adsorbed moisture in the sample. The amount of water (6 wt.\%, as shown in the Fig. S2 as the initial hump around 100 \degree C) is not considered for calculating SnO\textsubscript{2} amount in the final, dried SnO\textsubscript{2}-CMK-5 hybrid sample. From the TGA graph, measured SnO\textsubscript{2} amount is 38.4 wt.\% (including water content).
So, the calculated SnO$_2$ amount, based on excluding water content, is 40.9 wt. %. Therefore, this SnO$_2$ amount of 40.9 wt.% (excluding water), is used for calculating theoretical specific capacity of hybrid.

**EDX analysis of SnO$_2$-SBA-15 and SnO$_2$-CMK-5**

![Fig. S3](image_url)  
(a) Dark field TEM image of SnO$_2$-SBA-15 hybrid  
(b) EDX spectrum of selected area of SnO$_2$-SBA-15 hybrid [from Figure S2 (a)]  
(c) Dark field TEM image of SnO$_2$-CMK-5 hybrid  
(d) EDX spectrum of selected area of SnO$_2$-CMK-5 hybrid [from Figure S2 (c)].
Columbic efficiency of SnO$_2$, CMK-5 and SnO$_2$-CMK-5 electrodes

It is clearly seen from fig. S4 that the experimentally obtained columbic efficiency of first cycle is 55.8% for SnO$_2$-CMK-5, 40.5% for SnO$_2$ and 29% for CMK-5. From first cycle onwards, there is always an increase in columbic efficiency from 85 to 98% in all electrodes. The reason for lower columbic efficiency in the first cycle is irreversible capacity, which arises mainly due to SEI and Li$_2$O formation.

Fig. S4: Columbic efficiency of SnO$_2$, CMK-5 and SnO$_2$-CMK-5 electrodes

After the first cycle, columbic efficiency of all electrodes is drastically increased, due to negligible amount of further SEI formed in the subsequent cycles. However, it does not achieve up to 100% efficiency, as some SEI is still remaining. The above trend in the columbic efficiency plot is not only observed in the present case, but is also seen in other reports in the literature.$^{23}$
**Volume changes during lithiation/delithiation**

The empty space between the ordered mesopores helps SnO$_2$ nanoparticle to expand freely during the cycling process and also prevents electrode deterioration. The impact of CMK-5 during cycling is shown in fig where SnO$_2$ nanoparticles can expand along the mesochannels present in the CMK-5 during Li$^+$ insertion and contract during Li$^+$ extraction. Furthermore, CMK-5 channels can facilitate fast electron transport during the cycling process.

**Comparison of electrochemical performance of SnO$_2$-CMK-5 of our present work with other reports in the literature**

Table S1 above shows a comparison of cyclic performance of SnO$_2$-mesoporous carbon (CMK-5) with different forms of carbon based SnO$_2$ electrodes in recent studies. The entries in the above table have been arranged according to the following sequence of electrode materials: (i) nanostructured SnO$_2$ electrodes (ii) CMK electrodes and (iii) SnO$_2$-CMK-5 electrodes with different forms of carbon.
<table>
<thead>
<tr>
<th>Type of material</th>
<th>Current density (mAg(^{-1}))</th>
<th>Cycling Performance</th>
<th>Initial efficiency (%)</th>
<th>Voltage range (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>No of cycles</td>
<td>Reversible capacity (mAhg(^{-1}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO(_2) nanoparticles (~7nm)</td>
<td>178</td>
<td>30</td>
<td>42</td>
<td>40.5</td>
<td>Present work</td>
</tr>
<tr>
<td>SnO(_2) nanowire (~40 - 60 nm diameter; length more than 1(\mu)m)</td>
<td>782</td>
<td>50</td>
<td>510</td>
<td>37.4</td>
<td>[9]</td>
</tr>
<tr>
<td>SnO(_2) nanotube (180 nm diameter; 450 nm length)</td>
<td>100</td>
<td>30</td>
<td>468</td>
<td>40.4</td>
<td>[17]</td>
</tr>
<tr>
<td>Mesoporous carbon (CMK-3)</td>
<td>100</td>
<td>20</td>
<td>350</td>
<td>40.1</td>
<td>[18]</td>
</tr>
<tr>
<td>Mesoporous carbon (CMK-5)</td>
<td>178</td>
<td>30</td>
<td>218</td>
<td>29</td>
<td>Present work</td>
</tr>
<tr>
<td>SnO(_2)-mesoporous carbon</td>
<td>100</td>
<td>60</td>
<td>425</td>
<td>46</td>
<td>[22]</td>
</tr>
<tr>
<td>SnO(_2)-mesoporous carbon</td>
<td>100</td>
<td>100</td>
<td>593</td>
<td>65.3</td>
<td>[23]</td>
</tr>
<tr>
<td>SnO(_2)-mesoporous carbon</td>
<td>178</td>
<td>30</td>
<td>598</td>
<td>55.8</td>
<td>Present work</td>
</tr>
<tr>
<td>SnO(_2)-graphene</td>
<td>100</td>
<td>30</td>
<td>626</td>
<td>49</td>
<td>[13]</td>
</tr>
<tr>
<td>SnO(_2)-graphene</td>
<td>50</td>
<td>30</td>
<td>570</td>
<td>43</td>
<td>[12]</td>
</tr>
<tr>
<td>Carbon coated SnO(_2) nanotube</td>
<td>100</td>
<td>30</td>
<td>492.5</td>
<td>53.1</td>
<td>[16]</td>
</tr>
<tr>
<td>Mesoporous SnO(_2)-MWNT</td>
<td>33.3</td>
<td>50</td>
<td>345</td>
<td>74</td>
<td>[14]</td>
</tr>
<tr>
<td>Carbon coated mesoporous SnO(_2)</td>
<td>160</td>
<td>65</td>
<td>500</td>
<td>37.3</td>
<td>[8]</td>
</tr>
<tr>
<td>SnO(_2)/Ferrocene -SWNT</td>
<td>150</td>
<td>40</td>
<td>905</td>
<td>60</td>
<td>[10]</td>
</tr>
</tbody>
</table>
The objective is to highlight the most important parameters such as current density, reversible specific capacity, operated voltage range and initial efficiency. SnO$_2$ nanoparticles synthesized in the present work show poor reversible specific capacity ($42 \text{ mAh g}^{-1}$) in comparison to SnO$_2$-CMK-5 (598 mAh g$^{-1}$) and CMK-5 (218 mAh g$^{-1}$) electrodes synthesized in this work, at the same current density (178 mA g$^{-1}$). The reason for better reversible specific capacity in case of SnO$_2$-CMK-5 is that CMK-5 plays an important role in accommodating volume expansion during cycling performance.

In a recent report,$^9$ SnO$_2$ wire electrode showed reversible specific capacity of 510 mAh g$^{-1}$ after 50 cycles, at a current density of 782 mA g$^{-1}$, over an applied voltage of 0 - 1.2 V. The applied voltage range in the above report is less in comparison to other reports in literature,$^9$-18 which helps in achieving a high reversible specific capacity, at a high current density. Generally, capacity fading is drastic for the SnO$_2$ system, when it is operated above 1.3 V.$^{34}$ This phenomenon occurs mainly due to deterioration of Li$_2$O at 1.3 V. In the present work, stable cyclic performance is achieved over a wide voltage range of 0.002V-3V, confirming the value in adding CMK-5.

In a few reports,$^{12}$,$^{13}$ carbon coating or addition of other forms of carbon (graphene, carbon nanotube) is done with SnO$_2$ nanostructures, in order to accommodate volume expansion during cycling process. Among all carbon based SnO$_2$ electrodes in table S1, the performance of SnO$_2$-CMK-5 electrode is reasonably good, in terms of applied potential range, reversible capacity and current density.

In another recent report,$^{10}$ ferrocene was introduced inside a single wall carbon nanotube (SWNT) and subsequently SnO$_2$ nanoparticles were attached on ferrocene-SWNT hybrid. The role of ferrocene in the hybrid is that of an electron mediator. It shows slightly better performance (reversible specific capacity of 905 mAh g$^{-1}$, at a current density of
150 mA g\(^{-1}\) and initial efficiency of 60%), compared to the SnO\(_2\)-CMK-5 electrode synthesized by us, the latter has a reversible specific capacity 598 mAh g\(^{-1}\), at a current density of 178 mA g\(^{-1}\), and initial efficiency of 58.8 %.

**Theoretical specific capacity calculation**

**Present work**

A simple calculation is done to estimate the theoretical specific capacity of our synthesized SnO\(_2\)-CMK-5 electrode.\(^{22}\)

TS - Theoretical capacity of SnO\(_2\) (782 mAh g\(^{-1}\))

TC - Theoretical capacity of CMK-5 (430 mAh g\(^{-1}\))

MS – Wt. % of SnO\(_2\) (41%)

MC – Wt. % of CMK-5 (59%)

So, theoretical capacity of SnO\(_2\)-CMK-5 = ((TS x MS) + (TC x MC))

\[
= [(782 \times 0.41) + (430 \times 0.59)] \text{ mAh g}^{-1}
\]

\[
= 574.32 \text{ mAh g}^{-1}
\]

Now, the experimentally measured specific capacity of SnO\(_2\)-CMK-5 in the present work is 598 mAh g\(^{-1}\), which is slightly higher than the calculated theoretical capacity of 574 mAh g\(^{-1}\). This excess capacity contribution may be due to electrolyte decomposition (LiPF6). The above calculations are included in supplementary information of the revised manuscript.

**Other reports in the literature**

Similarly, if calculated, the theoretical capacity for the recent report on SnO\(_2\) - mesoporous carbon containing SnO\(_2\) (20 wt. %) and CMK-3 (80 wt. %).\(^{23}\) would be = 500
mAh g⁻¹, whilst their experimentally measured specific capacity of SnO₂-CMK-3 = 593 mAh g⁻¹, is somewhat less, just like our present work.

It is seen in another report²¹ that SnO₂-mesoporous carbon has specific capacity of 978 mAh g⁻¹ at a current density of 200 mA/g. Apart from this particular work, the observed specific capacity of SnO₂-mesoporous carbon in most of the reports⁸, ²², ²³ in literature is in the range of 400-600 mA h/g, at a current density of 100-200 mA h/ g. Our present work also shows a specific capacity at 598 mAh g⁻¹ at a current density of 178 mA g⁻¹, similar to literature. Therefore, the discharge capacity and current density values in the present work are not on the higher side.