Electronic Supplementary Information

Porous SnO$_2$/layered titanate nanohybrid with enhanced electrochemical performance for reversible lithium storage

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Theoretical capacity of STN. (Supporting information)

Lithium insertion reaction for the lepidocrocite-type layered titanate is as follows:

\[ \text{Ti}_{1.83}\text{O}_4 + x\text{Li} + xe^- \rightarrow \text{Li}_x\text{Ti}_{1.83}\text{O}_4 \]

where the maximum insertion coefficient, \( x \), is determined to be about 0.7.\(^1\) Thus, the theoretical capacity of the layered titanate could be calculated to 171 mAh/g.

The theoretical capacity of \( \text{SnO}_2 \) can be also calculated in the same way as the layered titanate. The reaction of \( \text{SnO}_2 \) with lithium is as follows:

\[ \text{SnO}_2 + 4\text{Li} \rightarrow \text{Sn} + 2\text{Li}_2\text{O} \]

\[ \text{Sn} + x\text{Li} \leftrightarrow \text{Li}_x\text{Sn} \]

The maximum theoretical capacity of the \( \text{SnO}_2 \) anode is determined to be 781 mAh/g by this mechanism.\(^2\)

Finally, the theoretical capacity of the hypothetical mixture between the layered titanate and the \( \text{SnO}_2 \) nanoparticle (\( C_{\text{theoretical}} \) for STN) was calculated by considering the \( C_{\text{layered titanate}} \) (171 mAh/g), \( C_{\text{rutile SnO}_2} \) nanoparticle (781 mAh/g), and the elemental ratio of both components in STNs (layered titanate : \( \text{SnO}_2 \) = 40% : 60%).

\( C_{\text{theoretical}} \) for STN is 537 mAh/g.
Supporting table

Table 1. Parameters obtained from N₂ adsorption-desorption measurements.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_{\text{BET}}^{a)}$ (m²/g)</th>
<th>$V_1^{b)}$ (mL/g)</th>
<th>Pore size$^{c)}$ (nm)</th>
<th>BDDT classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>STN-I</td>
<td>132</td>
<td>0.075</td>
<td>0.75</td>
<td>Type I</td>
</tr>
<tr>
<td>STN-II</td>
<td>177</td>
<td>0.104</td>
<td>2.4</td>
<td>Type I + IV</td>
</tr>
</tbody>
</table>

$^a)$ BET specific surface area calculated from the linear part of the BET plot.

$^b)$ Total pore volume (taken from the volume of N₂ adsorbed at about P/P₀ = 0.950).

$^c)$ The average pore diameter was estimated from the t-plot and the Barrett-Joyner-Halenda (BJH) formula for STN-I and STN-II, respectively.
Supporting figures

Figure S1. SEM images for (a) STN-I and (b) STN-II.

In the SEM images, the layered platelets morphology with several micrometer widths was observed for both STNs when viewed from the top. However, the SEM image from the edge side of STN-II, the layers are not well ordered, but rather randomly stacked, which is suggestive to the formation of house-of-card type porous structure. As the calcination temperature increased the external surface became smooth without forming any bulk deposition of SnO$_2$ nanoparticles, implying that the remarkable capacity fading arising from the volume expansion of SnO$_2$ nanoparticles may not occur during the first few Li insertion/extraction cycles in LIB application.
Figure S2. HR TEM images for (a) SnO$_2$ nanoparticles calcined at 250 °C and (b) SnO$_2$ nanoparticles calcined at 400 °C.
Figure S3. N\textsubscript{2} adsorption desorption isotherms for (a) restacked titanate, (b) STN-I, (c) SnO\textsubscript{2} nanoparticles, and (d) STN-II. The filled and open symbols represent adsorption and desorption data, respectively.

Little hysteresis loops indicative of the reversible N\textsubscript{2} adsorption/desorption process were observed for both STNs, implying that Li ion migration through the channels could be also reversible in electrochemical performance giving rise to the high cycling stability.\textsuperscript{3} This phenomenon would be attributed to the pores in STNs, which was controlled precisely by thermal treatment under Ar atmosphere.
Figure S4. Pore size distribution curve for (a) STN-I and (b) STN-II estimated from the t-plot and Barrett-Joyner-Halenda (BJH) formula (inset).

As plotted in the Figures for STN-I, no mesopores could be observed, but an average pore diameter of about 0.75 nm was obtained from t-plot extrapolation. However, STN-II contains mesopores with an average pore size of about 2.4 nm, which should be attributed to thermal decomposition of pore-blocking organic species after the heat treatment at 400 °C. In addition, it was observed that the mean size of micropores (about 1.1 nm) in STN-II was bigger than that in STN-I. As a consequence, STN-II could allow the access of Li ions and electrolyte molecules more easily than STN-I, which could result in a higher specific capacity.
Supporting references