Enhanced Charge-Discharge Properties of SnO2 Nanocrystallites in Confined Carbon Nanospace

Shinji Oro, Koki Urita and Isamu Moriguchi*

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

Much research work has been devoted to the development of energy storage devices with both high energy and high power densities due to expected demand for power-grid applications as well as power sources of electric and/or hybrid electric vehicle. Lithium-ion secondary batteries (LIBs) are attractive power storage devices, but they still need to be further improved for the power use. Enhancement of capacities and cycleability of electrode materials is one of the tactics to improve the LIB performance. With respect to the LIB anode materials, SnO2-based materials have been studied as a candidate of large capacity anode alternative to the present graphite or carbon anode. However, the electrochemical reactions of SnO2 with Li ions, which are composed of following reactions (1) and (2), are generally irreversible, and thus cause severe capacity fading during cycling.

\[ \text{Conversion reactions: } \text{SnO}_2 + 4 \text{Li}^+ + 4 e^- \leftrightarrow \text{Sn} + 2 \text{Li}_2\text{O} \quad (1) \]

\[ \text{Alloying/de-alloying reactions: } \text{Sn} + x \text{Li}^+ + x e^- \leftrightarrow \text{Li}_x\text{Sn} \quad (2) \]

Some researchers have tried to overcome the problem from the approaches of down-sizing of SnO2 particles\(^1\text{-}^5\) and controlling the morphology of SnO2 such as nanowires,\(^6\) nanotubes,\(^7\text{-}^8\) and nanospheres,\(^9\text{-}^12\) Some of them succeeded in yielding relatively high initial capacities, but the capacity retention was not improved enough due to cracking and crumbling in the SnO2-integrated electrodes caused by the volume change during Li insertion and extraction. Nanocomposites of SnO2 and carbon nanomaterials such as mesoporous carbons,\(^13\text{-}^15\) carbon nanotubes,\(^16\text{-}^17\) and graphene sheets\(^18\text{-}^20\) were effective to suppress the mechanical degradation and showed high capacities and a cycleability improved to some extent. The reported charge-discharge capacities of nanocomposites are including electric double layer capacities and/or Li intercalation/de-intercalation capacities of graphite phase, thus it is unclear how much the electrochemical reactions of SnO2 with Li ions contributed to the total capacities and the capacity retentions. In order to achieve high performance of SnO2 electrode materials, it is essentially important to clarify the reversibility of electrochemical reactions of SnO2 with Li ions and which structure is suitable for improving the performance.

Since the reported nanocomposites have heterogeneous structures where SnO2 nanoparticles are incorporated in irregular interspace and inner pores of carbon nanomaterials and also are deposited on the outer surfaces of them, it is difficult to evaluate exactly the SnO2 reactions affected significantly by the reaction space. In the present study, we have succeeded in almost perfect embedding of SnO2 nanocrystallites in the regulated carbon nanopores of ordered porous carbons for the first time, and have evaluated the reversibility of their electrochemical reactions. It is disclosed that the reversibility of charge-discharge reactions of SnO2 is greatly enhanced in the confined carbon nanospace.

Embedding of SnO2 nanocrystallites into nanopores of porous carbons was carried out by following two methods: [1] mixing of a nanoporous carbon with SnO2 sol in a solution, [2] introduction of SnCl2 vapor and conversion into SnO2 in the nanopores of nanomorous carbons. A nanoporous carbon with an average pore diameter of 120 nm, 45 nm or 18 nm, which was obtained by a silica opal template process as previously reported,\(^21\) was used for the above syntheses. Hereafter the porous carbon and the SnO2-embedded nanoporous carbon composites obtained by [1] and [2] methods are denoted as CX, SnO2/CX-sol and SnO2/CX-vap, respectively, where X indicates the average carbon pore size in nm. SnO2/C120-sol was obtained by mixing a SnO2·nH2O sol and C120 with the weight ratio of SnO2·nH2O/C120 = 85/15 in ethanol under a sonication for 6 h, followed by a filtration and a heating at 120 °C for 24 h.

SnO2 powder was also synthesized by heating a SnO2·nH2O sol in an O2 atmosphere (see experimental details in the ESI†).

The production of rutile-type SnO2 crystallites was confirmed by X-ray diffraction (XRD) measurements for all the samples (Fig. S1, ESI†). The primary crystallite size was estimated to be ca. 3 nm from the full width at half-maximum (FWHM) of the (110) XRD peak using the Scherrer equation. Table 1 shows structural parameters of SnO2 contents (\(W_{\text{SnO2}}\)), primary crystallite size of SnO2 (\(d\)), specific surface areas (\(S_a\)) and specific pore volumes (\(V_p\)) of samples, as well as weighted average values of \(S_a\) (\(S_{a,w}\)) and \(V_p\) (\(V_{p,w}\)) which are calculated under the assumption of a simple mixing of CX and SnO2 nanocrystallites.
with the primary crystallite size. The SnO$_2$ content of SnO$_2$/C-X-vap samples determined by thermogravimetry (TG) was 56 to 74 wt%, which corresponds to 68 to 90% conversion of SnCl$_2$ mixed with C-X. The $S_a$ and $V_p$ values of SnO$_2$/C-X samples were smaller than the values of $S_{aw}$ and $V_{pw}$, suggesting that SnO$_2$ nanocrystallites were produced preferentially in carbon nanopores.

It was actually observed by transmission electron microscopy (TEM) that SnO$_2$ nanocrystallites with the size of ca. 3 nm were deposited in nanopores of porous carbons for SnO$_2$/C-X-vap samples (Fig. 1). There were no agglomerated SnO$_2$ particles outside of porous carbons as far as we observed throughout. Porous surface without large agglomerated particles was also confirmed for SnO$_2$/C45-vap as a representative example by scanning electron microscopy (SEM) (Fig. S2, ESI†). If all of the SnO$_2$ nanocrystallites are located in the carbon nanopores, the wt% of SnO$_2$ in SnO$_2$/C-X-vap samples ($W_{\text{SnO}_2, \text{ calc}}$) can be calculated by using the following equations (3) and (4):

$$W_{\text{SnO}_2, \text{ calc}} = \frac{100x}{1 + x}$$

$$\rho = \frac{V_c - x}{V_p}$$

where $x$ is gram of SnO$_2$ per 1g of carbon in SnO$_2$/C-X-vap, $V_c$ and $V_p$ are specific pore volume of the SnO$_2$/C-X-vap and the original C-X, and $\rho$ is the density of SnO$_2$ crystal (6.95 cm$^3$ g$^{-1}$), respectively. The calculated $W_{\text{SnO}_2, \text{ calc}}$ were 76.8, 66.5 and 58.7 wt% for SnO$_2$/C120-vap, SnO$_2$/C45-vap and SnO$_2$/C18-vap, respectively, which are very close to the $W_{\text{SnO}_2}$ determined by TG measurements (Table 1). This demonstrates almost perfect embedding of SnO$_2$ nanocrystallites in nanopores of porous carbons for SnO$_2$/C-X-vap samples. On the other hand, agglomerated SnO$_2$ nanocrystallites were observed by TEM both in carbon nanopores and on the outer surface for SnO$_2$/C120-sol as shown in Fig. 1a. It can be concluded that in situ synthesis of SnO$_2$ with the introduction of vaporized Sn source is effective to deposit SnO$_2$ nanocrystallites dominantly in carbon nanopores.

Electrochemical measurements were carried out in a 1.0 mol dm$^{-3}$ solution of LiPF$_6$ in ethylene carbonate/dimethyl carbonate against metallic Li at room temperature. A mixture of SnO$_2$/C sample and poly(vinylidene difluoride) (PVDF) with the weight ratio of 90:10 were pressed on Ni mesh, and then were used as working electrodes. For the SnO$_2$ powder, 10 wt% of acetylene black (AB) was mixed as a conductive additive in the preparation of working electrode (See experimental details in ESI†). In the following, the SnO$_2$ electrode is denoted as SnO$_2$-AB. Fig. 2 shows cyclic voltammograms (CVs) of SnO$_2$-AB and SnO$_2$/C120-vap as representative examples. Redox peaks due to the SnO$_2$-Sn conversion reaction were observed around 1.2 and 0.9 V vs. Li/Li$^+$ in the cathodic sweep and around 1.1 and 1.9 V vs. Li/Li$^+$ in the anodic sweep. These peaks were remained on SnO$_2$/C120-vap even after 10th cycles in contrast that these peaks were almost disappeared for SnO$_2$-AB after the 2nd cycle, indicating that the reversibility of conversion reaction was improved for SnO$_2$/C120-vap. On the other hand, cathodic peak around 0.03 V and anodic peak around 0.6 V were ascribable to the redox of Sn-Li alloying and de-alloying reactions. The baseline current below 0.8 V was decreased and the change was almost saturated after the 2nd cycles, indicating that the alloying reaction at the initial cathodic sweep was accompanied with SEI formation. Because the redox peaks of alloying and de-alloying reactions for SnO$_2$/C120-vap were much larger and more stable than those for SnO$_2$-AB, the confinement of SnO$_2$ in carbon nanospace is also effective to enhance the reversibility of alloying.

### Table 1 Structural parameters of the samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$W_{\text{SnO}_2}$ (wt%)</th>
<th>$d$ (nm)</th>
<th>$S_a$ (m$^2$/g)</th>
<th>$S_{aw}$ (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_{pw}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$/C120-vap</td>
<td>74</td>
<td>3.2</td>
<td>258</td>
<td>517</td>
<td>0.23</td>
<td>0.38</td>
</tr>
<tr>
<td>SnO$_2$/C120-sol</td>
<td>66</td>
<td>3.0</td>
<td>265</td>
<td>588</td>
<td>0.35</td>
<td>0.50</td>
</tr>
<tr>
<td>SnO$_2$/C45-vap</td>
<td>62</td>
<td>2.4</td>
<td>379</td>
<td>602</td>
<td>1.42</td>
<td>1.72</td>
</tr>
<tr>
<td>SnO$_2$/C18-vap</td>
<td>56</td>
<td>3.3</td>
<td>575</td>
<td>700</td>
<td>2.04</td>
<td>2.26</td>
</tr>
<tr>
<td>C120</td>
<td>–</td>
<td>–</td>
<td>1174</td>
<td>–</td>
<td>1.47</td>
<td>–</td>
</tr>
<tr>
<td>C45</td>
<td>–</td>
<td>–</td>
<td>1093</td>
<td>–</td>
<td>4.53</td>
<td>–</td>
</tr>
<tr>
<td>C18</td>
<td>–</td>
<td>–</td>
<td>1229</td>
<td>–</td>
<td>5.15</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 1 TEM images of (a) SnO$_2$/C120-sol, (b) SnO$_2$/C120-vap, (c) SnO$_2$/C45-vap, (d) SnO$_2$/C18-vap, (e) the inner pore of SnO$_2$/C120-vap, and (f) the inner pore of SnO$_2$/C45-vap

Fig. 2 Cyclic voltammograms of (a) SnO$_2$-AB and (b) SnO$_2$/C120-vap during 1$^{st}$ to 3rd cycles
the charge capacities based on SnO\textsubscript{2} weight which was estimated around 100\% for SnO\textsubscript{2}/C\textsubscript{18-vap} during 30th cycling. On the other hand, the capacity retention of alloying reaction was almost constant Fig. 3a was confirmed on the SnO\textsubscript{2}-based capacities for the three discharge conditions (Fig. S4, SEI \textsuperscript{†}). The same tendency as in clearly indicate that the reversibility of alloying and de-alloying nanocrystallites in carbon nanopores is effective to improve not SnO\textsubscript{2}/C\textsubscript{120-sol} and SnO\textsubscript{2} with decreasing the pore size of C\textsubscript{18-vap} samples. These results indicate the confinement of SnO\textsubscript{2} and de-alloying reactions and SnO\textsubscript{2}/Sn\textsubscript{2+} reaction above 0.9 V than SnO\textsubscript{2}/C\textsubscript{120-sol} and SnO\textsubscript{2}. This journal is © The Royal Society of Chemistry [year] \textsuperscript{†} Electronic Supplementary Information (ESI) available: [Experimental details, XRD patterns of samples, SEM images of samples, initial charge-discharge curves of samples, charge-discharge properties of porous carbons, Coulombic efficiency, rate capability of samples, and cycle performance up to 100 cycles]. See DOI: 10.1039/b000000x/ and de-alloying reactions.

The charge-discharge properties were also evaluated by galvanostatic measurements. At the initial charge-discharge, the SnO\textsubscript{2}/C\textsubscript{120-vap} showed higher capacity of the conversion reaction above 0.9 V than SnO\textsubscript{2}/C\textsubscript{120-sol} and SnO\textsubscript{2}/AB although charge capacities in the potential range of 0.01 to 0.9 V due to de-alloying were almost the same (Fig. S3, SEI\textsuperscript{†}). As shown in Fig. 3a, the charge capacities based on the composite weight of SnO\textsubscript{2}/C\textsubscript{120 samples and SnO\textsubscript{2}/AB were decreased with cycling the charge-discharge, but the SnO\textsubscript{2}/C\textsubscript{120-vap was superior in the capacity retention to SnO\textsubscript{2}/C\textsubscript{120-sol} and SnO\textsubscript{2}/AB. Fig. 3b shows the charge capacities based on SnO\textsubscript{2} weight which was estimated by subtracting the capacities of C\textsubscript{45-vap} samples measured at the same charge-discharge conditions (Fig. S4, SEI\textsuperscript{†}). The same tendency as in Fig. 3a was confirmed on the SnO\textsubscript{2}-based capacities for the three samples. These results indicate the confinement of SnO\textsubscript{2} nanocrystallites in carbon nanopores is effective to improve not only the capacity but also the cycle performance. The Coulombic efficiency with cycling and the rate capability were improved by embedding the SnO\textsubscript{2} in carbon nanopores, too (Fig. S5 and S6, SEI\textsuperscript{†}). It was also found that the cyclability was greatly enhanced with decreasing the pore size of C\textsubscript{45} used for the synthesis of SnO\textsubscript{2}/C\textsubscript{45-vap} samples. The SnO\textsubscript{2}/C\textsubscript{18-vap showed the highest cyclability among the SnO\textsubscript{2}/C\textsubscript{45-vap} samples. The contribution of Sn-Li alloying and de-alloying reactions and SnO\textsubscript{2}/Sn\textsuperscript{2+} conversion reactions to the cycle performance was evaluated from these capacity retentions at the potential range of 0.01-0.9 V and 0.9-2.0 V, respectively (Fig. 3c, d). Surprisingly, the capacity retention of alloying reaction was almost constant around 100\% for SnO\textsubscript{2}/C\textsubscript{18-vap during 30th cycling. On the other hand, the capacity retention of conversion reactions for SnO\textsubscript{2}/C\textsubscript{18-vap was 73.4\% after 30 cycles, which is the highest value among those of SnO\textsubscript{2}/C\textsubscript{45-vap} samples. These results clearly indicate that the reversibility of alloying and de-alloying reactions as well as conversion reactions can be enhanced by embedding SnO\textsubscript{2} nanocrystallites in the confined carbon nanospace. Consequently, SnO\textsubscript{2}/C\textsubscript{18-vap showed excellent total capacity retention of 85.4\% after 30th cycles while keeping high capacities above 627 mAh g\textsuperscript{-1} of SnO\textsubscript{2}, which is higher than or comparable to the best performance reported on nanocomposites of SnO\textsubscript{2} and carbon materials except for graphene materials.\textsuperscript{14,16,23-26} The high capacity retention of SnO\textsubscript{2}/C\textsubscript{18-vap with cycling was preserved even after 100 cycles (Fig. S7, SEI\textsuperscript{†}). In conclusion, almost perfect embedding SnO\textsubscript{2} nanocrystallites into carbon nanopores were successfully achieved and the obtained nanocomposites showed excellent reversibility of Sn-Li alloying/de-alloying and SnO\textsubscript{2}/Sn\textsubscript{2+} conversion reactions. The regulation of reaction field in confined carbon nanospace is one of the key to enhance the charge-discharge properties of SnO\textsubscript{2}.

The study made use of XRD and TEM in the Center for Instruments Analysis of Nagasaki University. This work was partly supported by the Advanced Low Carbon Technology Research and Development Program of Japan Science and Technology Agency (JST) and a Grant-in-Aid for Scientific Research from Ministry of Education, Culture, Sports, Science and Technology of Japan.

Notes and references

Graduate School of Engineering, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521, JAPAN. E-mail: mrch@nagasaki-u.ac.jp

Fig. 3 Cycle performance in the potential range of (a, b) 0.01 to 2.0 V, (c) 0.01 to 0.9 V, and (d) 0.9 to 2.0 V. The charge capacities of (a) and (b-d) are based on the weight of composite materials and SnO\textsubscript{2}, respectively.