Electrochemical Properties of Disordered-Carbon-Coated SnO₂ Nanoparticles for Li Rechargeable Batteries

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The effects of carbon coating on ~9 nm SnO₂ particles were examined. The C-coated SnO₂ nanoparticles were synthesized from SnCl₄, glucose, and ethylene glycol through a solvothermal method. Raman spectra indicated that the coated carbon was a disordered carbon. The C-coated SnO₂ nanoparticles showed superior cycling properties to the uncoated ones. Transmission electron microscopy after cycling confirmed that the nanoparticles were well dispersed without aggregation. The enhanced cycling property is believed to be attributed to the effective hindrance of nanoparticle growth by the core/shell structure of Sn/Li₂O and carbon layer after phase separation during the first discharge.

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The ideal peak positions and intensities for rutile SnO$_2$ show superior cycling properties compared with the uncoated ones. In the C-coated SnO$_2$ nanoparticles, the relative intensity ratios (fitted with two Gaussian peaks) show typical disordered carbon. The larger local strain of the C-coated samples may be associated with the structural defects or a nonuniform distribution of strain by the carbon-coating surface. The Raman spectrum of the C-coated SnO$_2$ nanoparticles is shown in Fig. 1b. To know the bonding structure of the coated carbon, the spectrum was fitted with two Gaussian peaks.

Table I. The composition, size, and local strain of the uncoated and C-coated SnO$_2$ nanoparticles. The compositions were measured by ICP and CHNS analyses. The nanoparticle sizes were calculated by a Scherrer equation, and the local strains were acquired from the slope of $\Delta k$ vs $k$ plots.

<table>
<thead>
<tr>
<th></th>
<th>SnO$_2$ (wt %)</th>
<th>C (wt %)</th>
<th>H (wt %)</th>
<th>Size (nm)</th>
<th>Local strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>97</td>
<td>0.061</td>
<td>0.074</td>
<td>13.2 ± 1.1</td>
<td>0.13 ± 0.08</td>
</tr>
<tr>
<td>C-coated</td>
<td>90</td>
<td>4.9</td>
<td>0.35</td>
<td>8.8 ± 0.9</td>
<td>0.59 ± 0.13</td>
</tr>
</tbody>
</table>

Figure 1. (a) XRD patterns of the uncoated and C-coated SnO$_2$ nanoparticles. The ideal peak positions and intensities for rutile SnO$_2$ (ICPDS no. 41-1445) are marked at the bottom. (b) Raman spectra of the C-coated SnO$_2$ nanoparticles showing the bonding structure of the coated carbon. The relative intensity ratios (fitted with two Gaussian peaks) show typical disordered carbon.

Figure 2. TEM images of the C-coated SnO$_2$ nanoparticles with different magnifications. The arrowed region shows the SnO$_2$ nanoparticles surrounded by disordered carbon.

Figure 3. Cycle-life performance of the uncoated, C-coated SnO$_2$ nanoparticles, and disordered carbon as an active material, with the current rate of 500 mA/g (=0.64 C), between 5 mV and 1.2 V.
the oxidation of carbon leading to the release of CO₂ gas, and this result is comparable to the carbon concentration as shown in Table I by elemental analyzer.²⁵ It is believed that the slight weight loss below 300°C is caused by water or any organics.

The CV profile for the C-coated SnO₂ nanoparticles shows the suppression of Li₂O formation compared with the uncoated ones (see Fig. 6). This indicates some retardation of the decomposition reaction at the equilibrium-potential range. In addition, the cathodic and anodic peaks for LiₓSn alloy in the C-coated samples show larger polarization. Although there are a few reports related to these phenomena, the actual mechanisms are not fully understood.¹,⁸,¹⁴,²⁴ This may be because the charge mediation of the carbon-coating layer influences the overall change in the phase-transition kinetic. The TEM with a diffraction pattern for the C-coated SnO₂ nanoparticles at 1.2 V after 10 cycles shows that the tetragonal Sn phase Sn nanoparticles are well dispersed without much aggregation into larger Sn clusters (Fig. 7a). The Sn nanoparticles are surrounded by the arrowed dark-gray region, probably Li₂O and carbon layer, as shown in Fig. 7b. It is believed that the enhanced cycling property due to the carbon coating is attributed to the effective hindrance of the nanoparticle growth by the core/shell structure of Sn/Li₂O and carbon layer, after the phase separation during the first discharge.

Conclusions

The C-coated SnO₂ nanoparticles (~9 nm) were synthesized from SnCl₂, glucose, and ethylene glycol through a solvothermal method. Raman spectra indicated that the coated carbon was a disordered carbon. The C-coated SnO₂ nanoparticles showed the superior cycling properties compared with the uncoated one, and the capacity of ~500 mAh/g was maintained up to ~20 cycles. The TEM after cycling confirmed that the nanoparticles were well dispersed without aggregation. It is believed that the enhanced cycling properties by the carbon coating are attributed to the effective hindrance of the nanoparticle growth by the core/shell structure of Sn/Li₂O and carbon layer after the phase separation during the first discharge.

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