Investigation of anode materials for lithium-ion batteries

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CHAPTER 6. NOVEL SnO$_2$/PPy COMPOSITES AS LITHIUM ION BATTERY ANODES

6.1 Introduction

Recently, tin oxide and tin-based composite oxide electrodes have been investigated as possible negative electrodes for next generation lithium-ion batteries due to the desirable material properties of high capacity on both a gravimetric and a volumetric basis and the low potential of Li ion intercalation (Idota et al. 1997; Nam et al. 1999b). However, there is a large volume expansion and contraction problem associated with Li$^+$ insertion and removal reactions, respectively. Thus, mechanical stresses, related to the volume changes, induce a rapid decay in mechanical stability. The electrode suffers from cracking and crumbling ('pulverization’) as well as from consequent loss of electrode interparticle contact (Yang et al. 1996; Besenhard et al. 1997; Winter et al. 1998), resulting in the loss of capacity. Many efforts have been devoted to attempts to reduce the capacity fading. Courtney et al. (1999) used “spectator ions” (e.g. B$_2$O$_3$, P$_2$O$_5$) that do not undergo lithium alloying to create a dilution effect and keep the tin regions small. Several authors have combined tin or tin oxide with graphite and carbon in an attempt to reduce capacity fade (Lee et al. 2000b; Read et al. 2001). The approach has been to prevent the tin from becoming electrically disconnected through the use of a conductive matrix. Recently, conducting polymer polypyrrole has been studied as an additive to improve the performance of cathode and anode materials in lithium-ion batteries (Guo et al. 2005; Du Pasquier et al. 1999; Veeraraghavan et al. 2002b). The polypyrrole can work as a conducting matrix for the electrode particles. However, using polypyrrole powder as an additive to a tin based anode material in lithium-ion batteries has not been
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explored. In this study, SnO$_2$-polypyrrole composite was synthesised using a chemical polymerisation method, and the possibility of using SnO$_2$-polypyrrole composite as an anode materials for lithium-ion batteries was examined.

6.2 Synthesis and characterization of SnO$_2$/PPy composites

Nanostructured SnO$_2$ powder was synthesized using a spray pyrolysis technique. A 1.0 M SnCl$_2$ aqueous solution was used as the spray precursor. The SnO$_2$ powder was obtained using a vertical type of spray pyrolysis reactor at 700 °C. Then SnO$_2$-polyrrole (SnO$_2$-PPy) composites were prepared by a chemical polymerisation method with sodium p-toluenesulfonate (PTSNa) as the dopant and FeCl$_3$ as the oxidant. The molar ratio of monomer pyrrol to dopant was 3:1, and the molar ratio of monomer to oxidant was 1:3. Firstly, SnO$_2$ was dispersed into a solution of sodium p-toluenesulfonate and pyrrole. The mixture was stirred while the oxidation agent, FeCl$_3$ solution, was slowly added to the previous aqueous solution. The gradual change of color from light black to deep black indicated the formation of PPy. The reaction mixtures were then kept under the same conditions for 20 h. The total black mass was centrifuged, and then the mass was washed thoroughly with distilled water until free of FeCl$_3$. Finally, the black mass was dried at 50 °C for 4 hrs under vacuum. Adding appropriate weights of the monomer to 1g of the SnO$_2$ powder varied the polypyrrole content in the composites. Before polymerization, the monomer was distilled and guarded against exposure to light to prevent residual polymerization.
Fig. 6-1 presents the XRD pattern of SnO\textsubscript{2} powder synthesised by the spray pyrolysis method. It reveals the good crystalline tetragonal (p42/mnm) structure of the sample, and the peak positions agree well with JCPDS 41-1445. The average crystal size of the SnO\textsubscript{2} powder was determined by using the Traces program and the Scherrer formula. The average crystal size was about 5-15 nm.

The scanning electron micrographs of bare SnO\textsubscript{2} powder and SnO\textsubscript{2}-PPy composite are shown in Fig. 6-2(a) and (b), respectively. The SnO\textsubscript{2} particles are spherical agglomerates, around 1-2 microns in size. The SnO\textsubscript{2}-PPy composite shown in Fig. 6-2(b) indicates that the nanosize polypyrrole glues the SnO\textsubscript{2} particles together. To verify the formation of a composite of SnO\textsubscript{2}-PPy, EDS mapping analysis was used (see Fig. 6-2 (b) – (e)). The bright spots correspond to the presence of the elements Sn, N and C, respectively, in which the N and C are the elements of polypyrrole. The results show that N and C are
distributed uniformly throughout the whole area, which indicates that the polypyrrole particles had uniformly coated the surface of the SnO$_2$ powder.

Fig. 6-2 SEM images for (a) bare SnO$_2$ powder, (b) SnO$_2$-PPy (9.12 wt.% ) composite, and corresponding EDS mapping for image (b) as follows: (c) Sn mapping, (d) N mapping, (e) C mapping.
For quantifying the amount of PPy in the SnO$_2$-PPy composite materials, TGA analysis was carried out in air. The samples were heated from 50 °C to 800 °C at a rate of 5 °C min$^{-1}$. Fig. 6-3 shows the TGA analysis of the SnO$_2$-PPy composite samples along with those of bare SnO$_2$ and PPy powders.

Fig. 6-3 TGA curves of SnO$_2$-PPy composite, bare SnO$_2$ powder, and bare PPy powder.

As can be seen from Fig. 6-3, bare PPy powder burns off at 700 °C, while the bare SnO$_2$ powder remains stable in the temperature range used for this experiment. It can also be seen that the composites show weight loss over a temperature range of 300 to 700 °C, which corresponds to the oxidation of PPy. There is no further weight change in the composites after the initial oxidation of PPy. Therefore, the change in weight before and after the oxidation of PPy directly translates into the amount of PPy in the SnO$_2$-PPy composites. Using this method, it was found that the amounts of PPy in the composites were 9.12 wt.%, 18.25 wt.%, and 25.10 wt.% for the powders synthesized with various amounts of PPy, respectively.
6.3 Electrochemical properties of SnO$_2$/PPy composites

The CV curves of pure SnO$_2$ powder and SnO$_2$-PPy composite electrodes are shown in Fig. 6-4. The curves of the two samples are very similar. No additional peak was observed for the SnO$_2$-PPy composite. This suggests that polypyrrole was just acting as a conducting additive, and not as an active material contributing to the charge-discharge process.

![Cyclic voltammograms of the electrodes composed of bare SnO$_2$ powder and SnO$_2$-PPy composites.](image)

Fig. 6-4 Cyclic voltammograms of the electrodes composed of bare SnO$_2$ powder and SnO$_2$-PPy composites.

The initial cycle charging (Li intercalation) and discharging (Li deintercalation) curves are shown in Fig. 6-5. Note that the capacity is based on the total weight of the electrode. Although all the samples have shown some irreversible capacity losses, the amount of irreversible capacity loss of the SnO$_2$-PPy composites is much lower than that of the pure SnO$_2$. 
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Table 6-1 presents the irreversible capacity loss in the composites and the bare SnO$_2$ for various loading of PPy on SnO$_2$. From the Table, it can be seen that the initial irreversible capacity loss associated with bare SnO$_2$ is 69.2%, and that the amount of irreversible capacity loss decreases with increasing polypyrrole content. The PPy loading of 18.25% represents the optimum concentration, and any further increase in polypyrrole will add to the dead weight of the electrode, and consequently, to reduction in specific capacity.

Fig. 6-5 The charge/discharge profiles of the electrodes of bare SnO$_2$ powder and SnO$_2$-PPy composite.
Table 6-1. Initial irreversible capacity loss of the composites as a function of the polypyrrole content.

<table>
<thead>
<tr>
<th>Amount of PPy loading (wt.%)</th>
<th>Initial lithiation capacity (mAh/g)</th>
<th>Initial de-lithiation capacity (mAh/g)</th>
<th>Total irreversible capacity loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1851.6</td>
<td>570.0</td>
<td>69.2</td>
</tr>
<tr>
<td>9.12</td>
<td>1456.3</td>
<td>562.2</td>
<td>61.4</td>
</tr>
<tr>
<td>18.25</td>
<td>1191.7</td>
<td>562.0</td>
<td>54.0</td>
</tr>
<tr>
<td>25.10</td>
<td>1085.4</td>
<td>521.0</td>
<td>51.9</td>
</tr>
</tbody>
</table>

The tin dioxide reaction with lithium is a two-step process (Courtney and Dahn, 1997a). The first step in the irreversible reduction of SnO$_2$ results in the formation of tin regions dispersed within a Li$_2$O matrix. The second step is a lithium-alloying step that provides the reversible lithium storage capacity of these materials. The lithium-alloying step causes a large volume change in the Sn regions. As this material is cycled, the tin regions aggregate into larger regions. Even if the Li$_2$O matrix inhibits these tin regions from cracking, when the tin regions become too large, they cannot withstand the volume change and cracking occurs, resulting in a loss of capacity. In this work, the conducting polypyrrole polymer serves not only for dilution to prevent tin regions from aggregating, but also as a conducting matrix in which the SnO$_2$ particles are bound together (Veeraraghavan et al. 2002b) to prevent the tin from becoming electrically disconnected. This has been confirmed by SEM studies.

Morphological study of the electrodes after cycling shows that the cracks in the bare SnO$_2$ electrode are much larger than in the SnO$_2$-PPy composite electrode (Fig. 6-6). The discharge capacity vs. cycle number for the composite and bare SnO$_2$ electrodes are
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shown in Fig. 6-7. After 20 cycles, the SnO$_2$-PPy (18.25%) composite and bare SnO$_2$ electrodes remained at 70% and 40% of their initial capacity, respectively. The SnO$_2$-PPy composite shows a significantly improved cycle-life performance compared with the pure SnO$_2$.

Fig. 6-6 SEM images of electrodes. (a) bare SnO$_2$ electrode before cycling, (b) SnO$_2$-PPy composite electrode before cycling, (c) bare SnO$_2$ electrode after 20 cycles, (d) SnO$_2$-PPy composite electrode after 20 cycles.
Fig. 6-7 Discharge capacities vs. cycle number for the bare SnO\textsubscript{2} powder and SnO\textsubscript{2}-PPy composite electrodes.

6.4 Conclusion

A novel SnO\textsubscript{2}-PPy composite, suitable for lithium-ion battery anodes, was prepared by chemical polymerization. The conductive polypyrrole serves as a conducting matrix to buffer the active material in the composite and thus to reduce the volume change associated with Li\textsubscript{x}Sn alloying and dealloying reactions. The cyclability was improved compared to bare SnO\textsubscript{2} anodes.