Electrochemical properties of tin phosphates with various mesopore ratios

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Abstract

Tin phosphates with various mesopore ratios are synthesized with surfactants as templates. The mesopore ratios of the tin phosphates are controlled by adjusting the surfactant: inorganic precursor ratios. As an anode material for Li-ion batteries, the mesoporous and non-mesoporous mixture with a high mesopore ratio exhibits enhanced cycling stability. Compared with the ∼34% (∼135 mAh g⁻¹) capacity retention after 50 cycles of the non-mesoporous tin phosphate (between 2.5 and 0.001 V), the tin-phosphate anodes with mesopore ratios of 42, 82 and 100% show capacity retentions that are enhanced by more than 50%, showing charge capacities of ∼260, ∼290, and ∼325 mAh g⁻¹, respectively (after 50 cycles). The mesoporous structures may alleviate the large volume change of the Sn nanoparticles embedded in the lithium-phosphate matrix during charge–discharge. Cycling tests of the 100% mesoporous tin phosphate between 0.8 and 0.001 V exhibit no capacity decay: ∼325 mAh g⁻¹ remains after 50 cycles. This is probably because re-oxidation of metallic tin with lithium-phosphate matrix does not occur.

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Keywords: Energy storage; Electrochemical properties; Mesopore; Lithium-ion battery; Tin phosphate; Capacity retention

1. Introduction

The development of portable electronics and hybrid electric vehicles (HEVs) requires Li-ion batteries with high specific energy. Although commercially used graphite anodes have good electrochemical properties, their capacity (372 mAh g⁻¹ for LiC₆) is insufficient to satisfy the market requirements. Thus, tin-based anode materials such as metallic tin [1,2], tin oxides [3–5], and tin phosphates [6,7] have attracted much attention. Their theoretical capacities are two- or three-times larger (metallic tin: 959 mAh g⁻¹, SnO₂: 781 mAh g⁻¹ and Sn₂P₂O₇: 572 mAh g⁻¹, all for Li₄.4Sn) than that of graphite anodes. They have poor capacity retention however, due to their large volume change of over 300% during lithiation/delithiation. To enhance their capacity retention, mesoporous structures[8,9], which are generally synthesized using surfactants as templates and have pore sizes between 2 and 50 nm, have been applied to these tin-based materials [10–14].

The mesoporous structures of tin-based materials may act as buffer structures to alleviate the large volume change. Though tin-phosphate materials that consist of mesoporous and non-mesoporous composites have previously been studied [12–14], the effects of the mesopore ratio on their electrochemical properties remain unclear. In this study, tin phosphates with various mesopore ratios are synthesized, and their electrochemical properties examined.

2. Experimental

Tin phosphates with various mesopore ratios were prepared by mixing various amounts of SnF₂ and H₃PO₄, and dissolving them in 40 ml of distilled–deionized water. Then, 5.5 g of cetyl-trimethyl-ammonium bromide (CTAB: CH₃(CH₂)₁₅N(CH₃)₃Br) was dissolved in 20 ml of distilled–deionized water, and this solution was added to the SnF₂/H₃PO₄ solution. The molar ratio of SnF₂/H₃PO₄ was fixed at 1.35, while CTAB/H₃PO₄ molar ratios of 0.11, 0.22, 0.54 and 1.10 were prepared. The mixture was stirred at 40 °C for 1 h, loaded in an autoclave, and then kept at 90 °C for 24 h. After cooling to room temperature, the precipitates...
were recovered by centrifugal filtration, washed with distilled water and ethanol, and vacuum-dried at 100 °C for 10 h. The as-prepared powders were then annealed at 400 °C for 8 h to remove the CTAB surfactants [12].

Structural analyses were performed by means of X-ray diffraction (XRD: M18XHF-SRC, MAC Science) and small-angle X-ray spectroscopy (SAXS: Nanostar, Bruker) using Cu Kα radiation. Brunauer–Emmett–Teller (BET) surface areas and pore-size distributions were obtained from nitrogen isotherms measured at 77 K with an ASAP 2010 analyzer (Micromeritics). The composition of tin phosphate was characterized by inductively coupled plasma atomic-emission spectroscopy (ICP-AES: ICPS-7500, Shimadzu) and electron-probe microanalysis (EPMA: JXA-8900R, JEOL).

Electrochemical tests were performed with coin-type half-cells (2016 size) using lithium as an anode. The electrode consisted of 60 wt.% active materials, 20 wt.% Super P carbon black, and 20 wt.% polyvinylidene fluoride (PVDF). A mixture consisted of 60 wt.% active materials, 20 wt.% Super P carbon black, and 20 wt.% polyvinylidene fluoride (PVDF). A mixture of ethylene carbonate/diethylene carbonate (EC/DEC) with 1 M LiPF6 was used as the electrolyte. The cycling tests of the half-cells were carried out between 2.5 and 0.001 V (or between 0.8 and 144 mA g−1 afterwards.

### 3. Results and discussion

The tin phosphates synthesized with various CTAB/H3PO4 precursor ratios exhibit changes of mesostructures, as shown in Table 1. The d spacings of the mesopores were obtained from the SAXS measurements (Fig. 1(b)), and the average pore sizes were acquired using the Barrett–Joyner–Halenda (BJH) results from the nitrogen-adsorption isotherms. The relative mesopore ratios (in Table 1) were estimated from the measured pore sizes of the as-synthesized tin phosphates with various mesopore ratios, using Cu Kα radiation. Brunauer–Emmett–Teller (BET) surface areas and pore-size distributions were obtained from nitrogen isotherms measured at 77 K with an ASAP 2010 analyzer (Micromeritics). The composition of tin phosphate was characterized by inductively coupled plasma atomic-emission spectroscopy (ICP-AES: ICPS-7500, Shimadzu) and electron-probe microanalysis (EPMA: JXA-8900R, JEOL).

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#### Table 1

<table>
<thead>
<tr>
<th>CTAB/H3PO4 precursor molar ratio</th>
<th>Mesopore d spacing (nm)</th>
<th>Average pore size (nm)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Relative mesopore ratio (%)</th>
<th>Composition of synthesized Sn-P-O</th>
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<tr>
<td>0.11</td>
<td>~</td>
<td>~</td>
<td>14.7</td>
<td>0</td>
<td>Sn1.94P2O7.3</td>
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<tr>
<td>0.22</td>
<td>4.29 ± 1.21</td>
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<td>114</td>
<td>42</td>
<td>Sn2.61P2O7.8</td>
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<tr>
<td>0.54</td>
<td>4.34 ± 0.68</td>
<td>2.32</td>
<td>167</td>
<td>82</td>
<td>Sn2.72P2O8.1</td>
</tr>
<tr>
<td>1.10</td>
<td>4.20 ± 0.63</td>
<td>2.33</td>
<td>221</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

#### Fig. 1

(a) High-angle and (b) small-angle X-ray diffraction patterns of as-synthesized tin phosphates with various mesopore ratios, using Cu Kα radiation.
may interact with the CTAB surfactant to form a mesoporous structure. In contrast, the precursors unreacted with CTAB may form non-mesoporous Sn2P2O7 particles.

In the nitrogen-adsorption isotherms given in Fig. 3(b–d), the samples have a type IV isotherm [18], which means that they have a mesoporous structure. The BET surface areas of the tin phosphates are 14.7, 114, 167 and 221 m² g⁻¹ respectively, (Table 1), and the increase of the surface area correlates with the X-ray diffraction results (Fig. 1). From the nitrogen-adsorption isotherms, the pore-size distributions were obtained using BJH analysis. The average pore size in the annealed samples with mesopore ratios of 42, 82 and 100% is ∼2.56, ∼2.32 and ∼2.33 nm, respectively.

The voltage profiles of the tin-phosphate anodes with the various mesopore ratios are shown in Fig. 4. The non-mesoporous (0%) Sn2P2O7 anode delivers an initial discharge capacity of ∼780 mAh g⁻¹ including the irreversible capacity of ∼380 mAh g⁻¹ for the lithium-phosphate matrix such as Li3PO4 and LiPO3 [6]. Compared with the initial capacities (∼400 mAh g⁻¹) and capacity retention (∼85% after 5 cycles) of Ref. [6], the non-mesoporous (0%) Sn2P2O7 (Fig. 4) has a reasonable initial capacity and capacity retention with a high current rate and a wide voltage range. The plateau at ∼1.6 V during discharging may originate from the formation of a lithium-tin-phosphate matrix from the non-mesoporous crystalline tin-phosphate phase. The additional irreversible capacity beyond 260 mAh g⁻¹ for four Li⁺ ions (in Sn2P2O7) may be caused by the formation of a solid-electrolyte-interphase (SEI) layer [19].

As the mesopore ratio is increased, the tin content of the tin-phosphate anodes increases (shown in Table 1) and thus the capacity of the mesoporous tin phosphate is slightly increased. The initial discharge capacity of the tin phosphates with mesopore ratios of 42, 82 and 100% is 880, 1150 and 1220 mAh g⁻¹, respectively. (The capacities of the mesoporous tin phosphates are slightly lower than the values in Ref. [12], probably due to the different Sn-P-O ratios.) The irreversible capacity also increases with increasing mesoporous ratio (∼425, ∼590 and ∼660 mAh g⁻¹, respectively), probably because of the increased formation of an SEI layer due to the large surface area, and the formation of Li2O from over-supplied oxygen (Table 1). As shown in the insets of Fig. 4, the mesoporous tin-phosphate anode has a peak near 1.1 V (indicated by an arrow) during charge. This may correspond to the re-oxidation of the lithium-phosphate matrix, as in the case of the lithium-oxide matrix in SnO2 [20,21].

Fig. 5(a) shows the cycle-life performance (charging) of tin phosphates with various mesopore ratios between 2.5 and 0.001 V. As the mesopore ratio increases, the tin content also increases (as shown in Table 1) and thus the capacity
may become larger. Compared with the charge capacity of \( \sim 135 \text{ mAh g}^{-1} \) for the non-mesoporous (0%) tin phosphate after 50 cycles (\( \sim 34\% \) capacity retention of an initial capacity of \( \sim 400 \text{ mAh g}^{-1} \)), the samples with the mesopore ratios of 42, 82 and 100% exhibit improved capacity retentions of \( \sim 56, \sim 51 \) and \( \sim 58\% \) (\( \sim 260, \sim 290 \) and \( \sim 325 \text{ mAh g}^{-1} \)), respectively, for initial capacities of \( \sim 460, \sim 570 \) and \( \sim 560 \text{ mAh g}^{-1} \).

In contrast to the cycle-life performances, the SAXS peaks disappear after 50 cycles between 2.5 and 0.001 V (not shown). Though the mesoporous structures are preserved during the initial few cycles [12,13], the mesoporous characteristic seems to become disordered with increasing cycle number. Deteriorated mesoporous characteristics after 20 cycles have been reported in a previous study [14]. It seems that although the periodic mesoporous structures are destroyed, the contacts between the porous nanostructures remain without breakage. In cycling tests between 0.8 and 0.001 V (Fig. 5(b)), although the capacities decrease due to the limited charge cut-off, the cycling stabilities are greatly enhanced. It may be that the re-oxidation reaction (\( \sim 1.1 \text{ V peak} \)) of metallic tin with the lithium-phosphate matrix causes deterioration of the mesoporous structures and leads to poorer capacity retention, as in the case of the SnO2 system [20,21].

4. Conclusions

The mesoporous ratios of the tin phosphates are controlled by adjusting the ratio of surfactant to inorganic precursor. As an anode material for Li-ion batteries in cycling tests between 2.5 and 0.001 V, mesoporous tin-phosphate anodes with mesopore ratios of 42, 82 and 100% exhibit enhanced capacity retention of more than 50%. The corresponding discharge capacities are \( \sim 260, \sim 325 \) and \( \sim 290 \text{ mAh g}^{-1} \), as compared with the \( \sim 34\% \) capacity retention (\( \sim 135 \text{ mAh g}^{-1} \)) of the non-mesoporous tin phosphate. The mesoporous structures may alleviate the large volume change that occurs during charge–discharge, even though the mesoporous characteristics are destroyed after 50 cycles. The cycling tests of the 100% mesoporous tin phosphate between 0.8 and 0.001 V exhibit no decay of capacity, which remains at \( \sim 325 \text{ mAh g}^{-1} \) after 50 cycles.
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