Highly ordered mesoporous antimony-doped SnO₂ materials for lithium-ion battery

Gwi Ok Park*, Eunbyeol Hyung†, Jeong Kuk Shon†‡, Hansu Kim‡§ and Ji Man Kim*†¶
*Department of Energy Science
Sungkyunkwan University, Suwon 440-746
Republic of Korea
†Department of Chemistry
Sungkyunkwan University, Suwon 440-746
Republic of Korea
‡Department of Energy Engineering
Hanyang University, Seoul 133-791
Republic of Korea
§khansu@hanyang.ac.kr
¶jimankim@skku.edu

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Highly ordered mesoporous antimony-doped tin oxide (ATO) materials, containing different amount of antimony in the range of 0–50 mol%, are prepared via a nanoreplication method using a mesoporous silica template. The mesoporous ATO materials thus obtained exhibit high electrical conductivity, high reversible capacity, superior cycle stability and good rate capability as anode materials for lithium-ion batteries, compared to those of pure mesoporous tin oxide. Amongst the ATO materials in this work, the mesoporous ATO material with 10 mol% of antimony has highest discharge capacity of 1940 mAhg⁻¹ (charge capacity of 1049) at the 1st cycle, best cycle performance (716 mAhg⁻¹ at 100th cycle) and excellent rate capability, which are probably due to the enhanced electrical conductivity as well as reduced crystalline size.

Keywords: Lithium-ion battery; anode material; mesoporous; tin oxide; antimony-doped tin oxide.

1. Introduction

Tin oxide (SnO₂) has attracted considerable interests in the fields of Li-ion batteries as an alternative to a conventional graphite anode material due to the high theoretical capacity (790 mAhg⁻¹) and reasonably low reaction potential.¹–⁶ Unlike the intercalation mechanism of graphite anode for Li-storage, however, there is a large volume change...
during the charge and discharge process by conversion and alloy reaction of SnO2 anode with lithium.6 Practical implementation of SnO2-based anode is hampered due to such the large volume changes leading to fracture of electrode, loss of electric contact and poor cycle stability. Introducing the second metal element within the SnO2 framework is one of the breakthroughs to overcome the present problem. It could accommodate the volume changes, strengthen the mechanical stability by preventing from the integration of Sn particles and enhance the electrical conductivity.1,7–9 Antimony-doped tin oxide (ATO) exhibits high optical transparency, high electrical conductivity, good stability and low cost. Therefore, the ATO materials are useful for a wide range of applications such as transparent electrodes, heat mirrors, displays, rechargeable Li batteries and energy storage devices.10–18 Doping antimony is found to increase the electrical conductivity and mechanical stability of the SnO2-based material, thereby leading to improved electrochemical properties.19–21

The other strategy to improve cycle performance of SnO2-based anode is utilization of various nanostructured materials1–6,22–26 which have short diffusion pathlength for Li-ion and high surface areas facilitating Li-ion transport. Various kinds of nanostructured materials have been investigated as high-performance electrode materials for Li-ion batteries, including nanoparticles, one-dimensional (1D) nanostructures (nanorods, nanowires and nanotubes), and 2D nanostructures (nanobelts, and nanosheets), and 3D nanostructures (mesoporous materials). Among these nanomaterials, the mesoporous materials can provide a number of advantages. Mesoporous structure, which consists of several nanoscaled pores separated by walls of similar dimensions, retains short diffusion pathlength for Li-ion. The liquid electrolyte can easily flood into the mesopores, giving a high contact area with active frameworks. Ordered mesoporous materials also help in minimizing the wastage of pore volume, compared to the disordered porous material.27–30

In the present work, highly ordered mesoporous ATO materials were successfully obtained via a nanocasting method using a mesoporous silica template. The amount of antimony in the ATO materials was controlled in the range of 0–50 mol%. According to the best of our knowledge, this is the first application of ordered mesoporous ATO materials for the Li-ion battery. The mesoporous ATO anode materials exhibited high electrical conductivity, high reversible capacity, superior cycle stability and good rate capability, compared to pure mesoporous SnO2.

2. Experimental Section

2.1. Synthesis of mesoporous silica (KIT-6)

Mesoporous silica template with 3D mesostructure (KIT-6, cubic $Ia3d$ symmetry) was synthesized through the following method reported elsewhere.31 Triblock copolymer (Pluronic 123, EO$_{20}$PO$_{70}$EO$_{20}$, Aldrich, $M_{av} = 5800$) was used as a structure directing agent for KIT-6. Typically, 9.0 g of P123 and 9.0 g of n-butanol was dissolved in 326 g of doubly distilled water at room temperature. 17.7 g of concentrated HCl (Aldrich, 35 wt.%) solution was added to the above mixture with continuous stirring. After stirring for 1 h, 19.4 g of tetraethylorthosilicate (TEOS, 98%, Aldrich) was added into the solution under vigorous stirring at 308 K for 24 h, and subsequently the mixture was put in an oven at 373 K for another 24 h under static conditions. White precipitated product was filtered, washed with ethanol several times, dried in a 353 K, and finally calcined in air atmosphere at 823 K for 3 h.

2.2. Synthesis of mesoporous ATO materials

Tin(II) chloride (SnCl$_2$, 98%, Aldrich) and antimony(III) chloride (SbCl$_3$, 98%, Samchun) were used as the ATO precursors. Typically, 5.0 g of the KIT-6 was heated at 373 K for 1 h. The preheated KIT-6 was poured into a polypropylene bottle containing ATO precursors (3.5 g of SnCl$_2$ and 0–4.78 g of SbCl$_3$) and 1.61 g of hydrochloric acid (HCl, 35–37% Samchun). The bottle was closed and shaken vigorously for 1 h, in order to mix homogeneously the precursor solution with the KIT-6 template. Subsequently, the bottle was put in an oven at 353 K overnight for spontaneous infiltration of ATO precursor within the mesopores of KIT-6. The composite materials then were heated to 823 K under ambient atmosphere for 3 h. The silica template was removed by treating the composite material with an aqueous solution of HF (10 wt.%) three times. Finally, the mesoporous ATO material,
thus obtained, was washed with distilled water and acetone several times, and dried at 353 K for 24 h.
The Sb amount was controlled by mole percentages (Sb/(Sb + Sn)) in the precursor. The following nomenclature was used to describe the mesoporous ATO materials: meso-ATO-\(x\), where the \(x\) indicates the mol\% of antimony in the mesoporous ATO materials (\(x = 0, 10, 30\) and 50).

2.3. Characteristics

The meso-ATO-\(x\) materials were characterized by X-ray diffraction (XRD) with Cu\(K_\alpha\) X-ray source using a Rigaku D/MAX-III instrument. \(N_2\) adsorption–desorption isotherms were obtained using a Micromeritics Tristar at a liquid \(N_2\) temperature. Before the measurements, the materials were degassed for 12 h at 323 K. The Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to estimate the BET surface areas and BJH pore size distributions. Scanning electron microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDX) data were collected using LEO SUPRA 55 GENESIS 2000 instrument at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images were collected using a G2 FE-TEM at operating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained using ESCA 2000 (VG Microtech) instrument with Al\(K_\alpha\) (1486.6 eV) radiation. Measurements of sheet-resistance were carried out on a 4200 Keithley semiconductor characterization system. Before the sheet-resistance measurements, the mesoporous ATO-materials were mixed with cellulose and distilled water, and were pasted on slide glass. Then, the pastes were heated in air at 673 K to remove the cellulose.

2.4. Evaluation of electrochemical performance

The meso-ATO-\(x\) materials were mixed with Super-P carbon (MMM) as the conducting agent and polyvinylidene fluoride (PVDF) as the binder in N-methyl-2-pyrrolidone (NMP, Aldrich) solvent, for the electrochemical experiments. The weight ratio of ATO:Super-P:PVDF was 70:15:15. The slurry was spread onto a Cu foil current collector using a Doctor-Blade technique, and dried at 473 K under vacuum conditions. The electrodes thus obtained were cut into disks (12 mm in diameter). The electrochemical performance was conducted by assembling CR2016 coin cells, using Li metal as the counter electrode and Celgard 3501 as the separator. The electrolyte solution was 1.3 LiPF\(_6\) in a 3:7 v/v mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). Based on the current density of 70 mAg\(^{-1}\) (about 0.1 C), all the cells were tested within a fixed potential window (0.001–2.0 V) using a battery cycle tester (TOSCAT 4000 series, Toyo, Japan).

3. Results and Discussions

Figure 1 shows XRD patterns of the meso-ATO-\(x\) materials with different Sb contents. The low-angle XRD patterns [Fig. 1(a)] present well-defined peaks around \(2\theta = 1^\circ\), which correspond to the (211) reflection of the cubic \(Ia3d\) structure, indicating that highly ordered meso-ATO-\(x\) materials were successfully obtained from the KIT-6 template by the nanocasting method. Wide-angle XRD pattern in Fig. 1(b) exhibits several identified peaks at \(2\theta = 26.3^\circ, 33.8^\circ, 37.7^\circ\) and 51.7\(^\circ\), which can be assigned to (110), (101), (200) and (211) planes of cassiterite SnO\(_2\) structure (JCPDS card no. 88-0287). All the XRD peaks of meso-ATO-\(x\) were broadened with increasing the Sb content. The average crystallite sizes, determined by Scherrer’s formula to the (110) plane diffraction peak (\(2\theta = 26.6^\circ\)), decrease with increasing Sb content from 10.5 nm to 6.0 nm. It is clear that the existence of antimony within the SnO\(_2\) frameworks prevents from crystal growth of SnO\(_2\), leading to the decrease of crystallite size.\(^{13}\) No

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**Fig. 1.** (a) Low-angle and (b) wide-angle XRD patterns of meso-ATO-\(x\) (\(x = 0, 10, 30\) and 50) materials.
XRD peaks, originated from possible antimony compounds such as Sb$_2$O$_3$ or Sb$_2$O$_5$ in the form of separated domains, were observed. As listed in Table 1, lattice parameters of SnO$_2$ frameworks slightly decreased with increasing Sb content, which indicates that antimony elements are incorporated into the crystal lattice of SnO$_2$.

N$_2$ adsorption-desorption measurements are performed to further investigate the pore structure of the meso-ATO-$x$ materials. All the N$_2$ sorption isotherms for the meso-ATO-$x$ materials exhibit typical type-IV isotherms with hysteresis loops [Fig. 2(a)]. The physical properties of meso-ATO-$x$ materials are listed in Table 1. As shown in Fig. 2(b), the meso-ATO-$x$ materials exhibit dual porous structures (3–4 nm and about 20 nm). One should be originated from the silica frameworks of KIT-6 template (3–4 nm) after the nanocasting process, the other may be generated by the structural transformation from the cubic Ia$3d$ mesostructure to the tetragonal I$_41$/a (or lower) mesostructure.

SEM images for the meso-ATO-$x$ materials are presented in Fig. 3, indicating each particle is several micrometers of size (insets of Fig. 3). The highly ordered mesostructures on the surfaces of ATO particles are clearly observed, even though the overall morphologies of the meso-ATO-$x$ materials are irregular. There are also no detectable changes in morphology and size even for the meso-ATO-50 material. EDX data reveal the existence of Sn, O and Sb. No silicon and chlorine elements are detected, indicating that the silica template and the chloride derived from precursor were completely removed during the removal of silica template and the oxide formation. Despite the low accuracy to quantify the atomic contents based on the EDX analysis due to the close L radiation of Sn and Sb elements, the observed elemental compositions of Sn and Sb well agree with the calculated ones from the ratios in precursor solutions.

TEM images of the meso-ATO-0 and meso-ATO-10 are shown in Fig. 4. The ATO-$x$ materials exhibit well-distinguishable mesostructures and highly crystalline frameworks, indicating the successful replication from the KIT-6 template. The framework thicknesses are about 7 nm which are very similar to those estimated by Scherrer’s equation from the XRD patterns. The well-defined mesopores of ATO-$x$ materials may lead to better cycling performance, relieving that the strain caused by electrochemically induced volume change upon cycling.

The electrical resistances for the meso-ATO-$x$ materials, measured by the four-probe method, are

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### Table 1. Physicochemical properties of meso-ATO-$x$ materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\alpha_0$ (Å)</th>
<th>$S_{BET}^a$ (m$^2$g$^{-1}$)</th>
<th>$V_{\text{tot}}^c$ (cm$^3$g$^{-1}$)</th>
<th>$D_{\text{BJH}}^d$ (nm)</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$W_{\text{XRD}}^e$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>meso-ATO-0</td>
<td>20.79</td>
<td>84</td>
<td>0.34</td>
<td>3.1</td>
<td>4.740</td>
<td>3.192</td>
<td>10.5</td>
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<tr>
<td>meso-ATO-10</td>
<td>21.20</td>
<td>100</td>
<td>0.31</td>
<td>3.0</td>
<td>4.738</td>
<td>3.190</td>
<td>8.5</td>
</tr>
<tr>
<td>meso-ATO-30</td>
<td>20.99</td>
<td>110</td>
<td>0.33</td>
<td>3.1</td>
<td>4.732</td>
<td>3.180</td>
<td>6.6</td>
</tr>
<tr>
<td>meso-ATO-50</td>
<td>20.79</td>
<td>142</td>
<td>0.38</td>
<td>3.8</td>
<td>4.727</td>
<td>3.178</td>
<td>6.0</td>
</tr>
</tbody>
</table>

$^a$Unit cell parameters obtained from the low angle XRD patterns.

$^b$Specific surface areas calculated by the BET method.

$^c$Total pore volume measured at $p/p_0 = 0.99$.

$^d$Mesopore diameter obtained by BJH method.

$^e$Crystallite size calculated by the Scherrer’s formula to the (110) plane diffraction peak ($2\theta = 26.6^\circ$). Lattice parameters of crystalline frameworks were obtained from the ATO materials with various Sb contents.
presented in Fig. 5(a). It is depicted that the electrical resistance drastically decreases when the antimony content is 10 mol% ($7.1 \times 10^2 \Omega$), compared to that of meso-ATO-0 ($1.9 \times 10^6 \Omega$). The sheet resistances of meso-ATO-$x$ materials increase again after 10 mol% of Sb doping. It is well-known that conductivity of the ATO materials is dependent on the Sb content and its oxidation state in...

Fig. 3. SEM images for (a) meso-ATO-0, (b) meso-ATO-10, (c) meso-ATO-30 and (d) meso-ATO-50. The insets are the corresponding SEM images on low-magnification range.

Fig. 4. TEM images for (a) meso-ATO-0 and (b) meso-ATO-10. The insets are the corresponding HRTEM images.
The conductivity mechanism of the ATO material is deeply related to the co-existence of both Sb$^{3+}$ and Sb$^{5+}$ oxidation state. While the Sb$^{5+}$ ions act as electron donors, forming a shallow donor level close to the conduction band of SnO$_2$, the Sb$^{3+}$ ions behave as electron acceptors. Therefore, the change of conductivity upon different Sb contents in the present meso-ATO-$x$ materials is ascribed to the change of Sb$^{5+}$/Sb$^{3+}$ ratio. To gain further insights on the relationship between the electrical conductivity and the oxidation state of Sb, XPS experiments were carried out for the meso-ATO-$x$ materials. Figure 5(b) presents the XPS spectra of Sb 3d and O 1s core levels for the meso-ATO-10 and 50. Deconvolution data of the Sb 3d$_{3/2}$ peaks (c) meso-ATO-10 and (d) meso-ATO-50.

The electrochemical performance of the meso-ATO-$x$ materials was investigated as the anode materials for Li-ion battery. Figures 6(a) and 6(b) show the voltage profiles of the meso-ATO-0 and meso-ATO-10 for the 1st, 2nd, 3rd, 10th, 30th and 50th cycles at a constant current density of 70 mAg$^{-1}$ within a cut-off potential window of 0.001–2.0 V versus Li/Li$^+$. The meso-ATO-0 represents an initial discharge capacity of 1948 mAhg$^{-1}$ and charge capacity of 1120 mAhg$^{-1}$, which is quantitatively similar to meso-ATO-10.
Figures 6(c) and 6(d) show the corresponding differential capacity versus potential plot for the 1st, 2nd, and 3rd to gain further insights on the reaction of the meso-ATO-\(x\) materials. The large cathodic peak for the 1st cycle in the range of 0.8–1.1 V versus Li/Li\(^+\) corresponds to the SEI formation and the reaction between SnO\(_2\) and Li-ion, leading to the formation of both Sn and Sb metal and the Sn–Sb alloy in the Li\(_2\)O matrix (conversion reaction). For the meso-ATO-10 material, the dissociation of the oxide takes place at higher potential and the peak is broader than that of the meso-ATO-0 material. During the subsequent cycle, the reduction peaks of meso-ATO-\(x\) materials shift to 0.9 V versus Li/Li\(^+\) and reduced drastically. It indicates that irreversible reaction occurs in the initial cycle and the conversion reaction of meso-ATO-\(x\) materials is partially reversible. The pronounced cathodic peak and anodic peak are observed at the potential of 0.2 V and 0.5 V in the prolonged cycle, corresponding to the reversible alloying and dealloying processes, respectively. It indicates that the meso-ATO-0 and meso-ATO-10 behave in the same electrochemical pathway and also consistent with the previous reports.\(^{20,35}\)

The initial efficiency and discharge–charge capacity are a little lower than those of the meso-ATO-0 material, probably due to the presence of Sb. However, a reversible capacity of the meso-ATO-10 is 782 mAhg\(^{-1}\) at 50th cycle, whereas the meso-ATO-0 material gives 674 mAhg\(^{-1}\) at 50th cycle. The enhanced electrochemical performance, especially the cycling behavior, might be attributed to the increased electrical conductivity and the reduction of the strain originated from the electrochemically induced volume change by the Sb doping.

Comparison of the charge cycling performances of the meso-ATO-\(x\) electrodes is represented in Fig. 7(a). The meso-ATO-0 electrode exhibits high charge capacity of 1120 mAhg\(^{-1}\) at the first cycle, but the capacity decays drastically and reaches 553 mAhg\(^{-1}\) at 100th cycle (50% cycle retention at 100th cycle). However, the Sb-doping results in improved cycle performances, even though the capacities at the 1st cycle are slightly lower than that of the meso-ATO-0. Especially, the meso-ATO-10 electrode shows 716 mAhg\(^{-1}\) at 100th cycle (67% cycle retention). In general, poor cycling stability is inevitable for the SnO\(_2\)-based system due to the impressive electrochemically induced volume changes during prolonged discharge–charge process. However, the capacity of meso-ATO-10 electrode does not fade significantly upon cycling, which is attributed to the presence of Sb. Antimony-doping clearly influences the crystal growth of SnO\(_2\) as shown in Table 1. In addition, it is well known that the presence of the doping element in the Li–Sn alloy favored the Sn atom dispersion. The improvement in capacity during cycle could be attributed to the prevention of the large crystal growth during cycle as result of antimony doping, which is helpful for improving mechanical reversibility. The existence of Sb in the meso-ATO-\(x\) materials increases the rate capability. As shown in Fig. 7(b), the multi-current density charge cycling is conducted for three cycles each from C/20 to C/10, C/5, C/2, 1C and C/5 in stages to investigate the rate capabilities. As the charge/discharge rate increases, the capacities of the meso-ATO-0 electrode decrease from 100 to 85, 75, 64, 54 and 74%, respectively [Fig. 7(b)], whereas the meso-ATO-10 electrode gives the capacities from 100 to 93, 85, 73, 62 and 79%. The better rate capability of the meso-ATO-10 electrode in this research can be attributed to the excellent electrical conductivity upon Sb doping.

4. Conclusions

Highly ordered mesoporous ATO materials were successfully synthesized from the mesoporous silica template. The electrical conductivity of meso-ATO-10 is drastically enhanced, compared to that of meso-ATO-0. Moreover, the Sb-doping results in the high capacity retention (67 at\% 100th cycle) as well as excellent rate capability. We believe that the Sb doping reduces the possibility of aggregation of metallic tin toward larger crystals and accommodates...
the electrochemically induced volume change during Li alloying–dealloying process.

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