METAL ORGANIC COMPOSITES DERIVED TIN DIOXIDE/C
NANOPARTICLES FOR SODIUM-ION BATTERY

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METAL ORGANIC COMPOSITES DERIVED TIN DIOXIDE/C
NANOPARTICLES FOR SODIUM-ION BATTERY

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Thesis

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ABSTRACT

Tin-based materials, performing high theoretical capacity, have been regarded as one of the most promising alternative anode materials for sodium-ion battery (SIB). Tin and its derivative composite materials including SnO2 and SnO are subjected to serious volume expansion for SIB applications. In order to counter the problem, tin-based materials are usually pulverized into ultra small particles, and then coated with carbon layers to accommodate volume expansion as well as to prevent aggregation. The metal organic composites was chosen and utilized as the strategy to fulfill the required conditions. The goal composites were fabricated by hydrothermal reaction and annealed to obtain SnO2/C nanoparticles. Subsequently, a series of characterization such as scanning electron microscopy (SEM), and transmission electron microscopy (TEM)... were carried out to confirm materials’ morphology. Further galvanostatic charge/discharge and cyclic voltammograms electrochemical characterizations were tested upon the fabrication of SIBs. The SIB delivered high reversible capacities of 262 mAh/g and 200 mAh/g at 500 mA/g and 1A/g, respectively. The carbon layers coating mitigate the volume expansion and help to prevent aggregation as well as improve the conductivity. Final results from electrochemical performances provided the evidence that the SnO2/C nanoparticles could be an excellent anode material candidate for SIB system.
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CHAPTER I

INTRODUCTION AND BACKGROUND

1.1 Renewable Energy

With the awareness of environmental protection, people now tend to utilize some renewable green energy instead of traditional energy like fossil energy. Usually, renewable energy comes from nature phenomena such as sunshine, wind, waster, tide and geotherm without creating any pollution or wasting\(^1\). And for traditional fossil energy, it would produce a large quantity CO\(_2\), one of the main greenhouse gases, and cause server global warming year-by-year if fossil energy is still the main energy in our daily life. In the past 50 years, the content of carbon dioxide in the air increase with the rate 0.25 ± 0.21%/year\(^2\).

![Image of CO\(_2\) concentration in atmosphere from 650,000 years ago to near present, according to ice core proxy data and direct measurements\(^3\).](image-url)

Figure 1.1-1 CO\(_2\) concentration in atmosphere from 650,000 years ago to near present, according to ice core proxy data and direct measurements\(^3\).
Figure 1.1-1 show the CO₂ concentration in the atmosphere from about 650,000 years to current, indicating the tremendous change in the air and causing the greenhouse effect. And scientist estimated temperature would reach the historical value at about 2047 with current increasing rate, bringing harmful effect to ecosystems as well as people’s daily life⁴. Therefore, people now focus on alternative energy sources. And solar energy and wind energy are treated as promising energy sources.

For the solar energy, it has been utilized for a long time. Generally, solar energy was collected to use in two ways. The first one is to transfer to thermal energy to heat water and cook food, which was mostly used in poor areas with little resources. Another one is to transfer to electricity for further uses. According to some reports, in 2006, the annual potential of solar energy was estimated to be around 3,850,000 EJ while the whole electricity consumption was only 67 EJ⁵. Obviously, it could be a huge resource to satisfy our daily consumption if we can make use of this energy in a high efficient way.

Figure 1.1-2 World energy consumption by source. Renewables accounted for 19% in 2012⁶.
However, as shown in Figure 1.1-2, though solar energy is such a huge energy source, fossil fuels still occupies more than 80% in the world energy consumption in 2010 due to difficulties in collecting and utilization in solar energy. But with the further study in solar cell and energy collecting techniques, the occupation of solar energy would increase in the future.

For another promising renewable energy, wind energy, is suffering some similar problems in utilization. Wind energy collecting was first used in 19 century and now utilized almost in every county, as one of the clearest and easy to collect renewable energy. Also, unlike solar energy, wind energy could be collected 24 hours in every season.

![Figure 1.1-3 Global annual new installed wind capacity 1997-2015.](in MW)

Based on the data from ‘Global Wind Statistics’, from 1997-2015, wind energy storage increased year by year. A lot of countries have built up many wind farms and taken advantage of this energy. For example, in China, energy with more than 186 TWh
was created in 2012. And the most powerful wind farm in China could possess more than 6000 MW. Especially, more than 40% energy was produced from wing energy in Denmark. It is believed that both kinds of renewable energy will be more widely used in the future. In addition, in order to improve the energy collecting efficiency, wind energy as well as solar energy would usually combine with each other to build multi-functional power stations.

1.2 Sodium-based Batteries

Since renewable energy studies are on a hot spot and popular in energy development, beside the gathering techniques, energy storage techniques are of importance. Unlike traditional fossil energy, both solar energy and wind energy are strongly limited by topography and seasonal factors. In other word, renewable energy is unstable and fluctuates all the time as a kind of intermittent energy source. Thus, it is not possible to connect to our current energy system directly. And energy storage is necessary and significant in renewable energy applications.

For the current energy storage systems, there are three types strategies. The first one is the mechanical energy storage, including flywheels and compressing air methods, which was not able to reach current requirements due to high cost as well as low efficiency. The second one is the thermal storage, which is also limited by the working temperature. And the final one is the most widely use method, the electrochemical storage. Over, electrochemical storage technique is safer, cheaper and more stable than mechanical and thermal storage strategies. Usually, it contains several types battery systems. The first one was the lead-acid battery, one of commercial cells. Because of
low price and historical reason, it is widely used in our daily life. However, it has a very low electrochemical performance and a huge environmental problem when using heavy metal in batteries. Thus, it is not proper to be used in large energy station. The second one is the flow cell, which is difficult to design and construct. The final one is the lithium and sodium based batteries.

Lithium-based battery is the most popular commercial cell in the market due to outstanding electrochemical performance. But the content of lithium element in earth’s crust is barely 1.80 E-5 and the prize is every high with about 30 USD Ib⁻¹ which limit further application. Therefore, scientists focus on alternative materials. Among these alternative candidates, sodium-based battery draws a lot attention. The content of sodium in ear’s crust is around 2.27 E-2 and the prize is very low. Though electrochemical performance of sodium-based battery is not as well as the lithium battery shown in the Figure 1.2-1, electrochemical performance is not the important point in energy station. For energy station, it only considers the cost, safety and whether it can be build in large-scale. From this perspective, sodium-based battery is the better choice.

According to the data about Sodium versus Lithium characteristic, both size and density of lithium atoms are very small compared to sodium atoms. Also, electrochemical performance lithium is much better than sodium, like the capacity (3829 mAh/g compared to 1165 mAh/g). However, as an alternative battery, sodium is much cheaper than lithium, about more than 30 times cheaper. Moreover, sodium is more stable than lithium due to higher voltage compared to standard hydrogen electrode. For sodium-based batteries, they also suffer from some shortages. Because sodium ions are larger than lithium ions, sodium ions would be more difficult to intercalate between electrodes when under charge/discharge process. Therefor, it limits choices of cathode
anode host materials just based on the intercalation mechanism in lithium-based battery systems\textsuperscript{13}. Also, the melting point of metallic sodium is around 98 °C\textsuperscript{15}, which means it is nor proper to use metallic sodium as working electrode in commercial cells. Overall, scientists focus on finding outstanding cathode and anode electrodes.

1.3 Anode materials

Usually, for anode materials, there are three types. The first type is the carbon-based anode material, such as the graphite\textsuperscript{16}, carbon fiber\textsuperscript{17} and hard-carbon\textsuperscript{18}. However, for carbon-based anode materials, it shows poor electrochemical performance and fast loss in reversible capacity. Second type is intermetallic anode material, like SnSb\textsuperscript{19}. The third type is the metal oxide anode material, like SnO\textsubscript{2}\textsuperscript{5,20}, TiO\textsubscript{2}\textsuperscript{21} and NiCo\textsubscript{2}O\textsubscript{4}\textsuperscript{22}. TiO\textsubscript{2} materials usually show low electrochemical performance (less than 300 mAh/g). And metallic Co materials are very expensive (10-25 $US/lb) which limits widely used in commercial cells. For Sn-based anode material, it is batter than other anode materials on matter in price or electrochemical performance. Thus, Sn-based material is the research point in this thesis.

Figure 1.3-1 Schematic illustration of the structural revolution of Sn nanoparticles during sodiation.\textsuperscript{23}
As the most obvious advantage, the metallic Sn is very cheap, roughly 5-15 $US/lb$ which indicates that it could be widely used in further applications in the future. Based on reports in Sn materials in both lithium and sodium batteries, shown in Figure 1.3-2, the reversible reaction between sodium and tin belongs to type B conversion, which is a solid-state reaction during sodiation/desodiation. And the capacity of this reaction is about 847 mAh/g. Besides, this alloy mechanism can also help to reduce dendrite formation, which can cause short circuit and destroy separator in cells, by improving compatibility between alloy and electrolyte solvent. However, the pure Sn materials are difficult to fabricate in order to obtain good performance. Instead, SnO$_2$ materials are usually synthesis to use in batteries as anode materials. But SnO$_2$ materials do not have any capacity and they would react with sodium ions and reduce into metallic Sn. And then it would continue this reversible reaction. So, there will be capacity loss in the very beginning and combined capacity is around 667 mAh/g.

\[
\text{Sn} + 3.75\text{Na}^+ + 3.75\text{e}^- \leftrightarrow \text{Na}_{3.75}\text{Sn}
\]

Figure 1.3-2 Reversible reaction of Sn in sodium-based battery.

To elevate Sn-based electrode performance, several strategies are utilized. Shown in Figure 1.3-1, during the alloying process, the size of the final Na-Sn alloy is about 4 times as large as the original materials, which means it will go through the large volume expansion in the charge/discharge process. And under such volume expansion, alloy materials are very easy to crush and decrease the performance. Also, when those SnO$_2$ turn into metallic Sn, they will easily aggregate together and make the volume expansion
problem more serious. In order to accommodate this problem, SnO$_2$ materials are usually made into very small, which can buffer the volume changing, and cover some carbon layers to prevent the aggregation problem. In addition, carbon-based materials will be added to the system at the aim to improve the conductivity. To satisfy these requirements, methods, like ball milling$^{26}$, hydrothermal$^{27}$, solvothermal$^{28}$, gas-deposition$^{29}$, were utilized. For this thesis, hydrothermal method was used to synthesis the metal organic composites as the precursor. And then the precursor materials would be annealed to obtain the final product.
CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

All materials were used as received without further purification. Tin(IV) chloride (anhydrous, 98% STREM), N-methyl-2-pyrrolidone (NMP, 99.5% EMD), ethanol (200 proof, Decon Laboratories, Inc.), ethylene carbonate (EC, 99.9% Sigma-Aldrich), propylene carbonate (PC, 99.7% Sigma-Aldrich), sodium (99.8% Acros), were used as received without further purification. Poly(acrylic acid) (PAA, Mw = 450000) were purchased from Scientific Polymer Products, Inc. and used as received. Copper foil was obtained from MTI Corporation and the thickness was 9 μm.

2.2 Instrumentation and Instrumental Techniques

Scanning Electron Microscopy (SEM) (JOEL, JSM-7401F) and Transmission Electron Microscopy (TEM) (JEOL, JSM-1230, operated at 120 kV), X-ray diffraction (XRD) Rigaku Ultima IV X-ray diffractometer equipped with Cu Kα radiation (λ=1.5604Å), Thermogravimetric analysis (TGA) Q500 (TA Instruments), X-ray photoelectron spectroscopy (XPS) PHI VersaProbe II Scanning XPS Microprobe.
2.3 Synthesis

There will be 2 steps in the synthesis section. The first part is using hydrothermal reaction to synthesis the metal organic composites as the precursor materials for further annealing process. In the second part, precursor materials would be annealed in the CVD furnace to obtain the final product.

2.3.1 Synthesis of Sn-MOFs

100 mg SnCl4 (anhydrous), 192 mg terephthalic acid were uniformly dissolved in a 30 mL mixture solution (DMF : ethanol = 1:1 v/v) by magnetic stirring treatment. The mixed precursor solution was then poured into a Teflon-lined autoclave (50 mL in capacity) and heated at 150°C for 12 h. The precipitates were collected via centrifugation at 4400 rpm for 10 min, and then washed with pure ethanol several times. The product was then dried at 80°C overnight in oven.

2.3.2 Synthesis of SnO2/C nanoparticles and bare SnO2 nanoparticles

SnO2/C nanoparticles were obtained from precursor materials via calcination treatment, which completely carbonized the carbon ligand as well as oxidized SnO2, under 500°C for 2h in Ar atmosphere. For comparison, the SnO2/C nanoparticles were then heated under 500°C for 2h in air in order to eliminated carbon and obtained bare SnO2 nanoparticles.
2.4 Cell assembly and electrochemical measurements

To prepare electrodes, the as-prepared SnO$_2$/C nanoparticles (70 wt%), poly(acrylic acid) binder (PAA, 10 wt%), and carbon black (20 wt%) were well mixed (50 mg in total) and dispersed into N-methyl-2-pyrrolidone (NMP, 0.6 mL) to form a slurry. Then, the slurry was cast on a smooth copper foil by using doctor blade and dried in oven at 80°C overnight. In contrast, bare SnO$_2$ nanoparticles were used to prepare another electrode by the same process. The working electrodes were obtained by punching the dried electrode film into discs with a diameter of 7.98 mm. The coin-type (CR2032) half cells were assembled in an Ar-filled glove box where water and oxygen were less than 1 ppm. The metallic sodium foil was applied as both counter electrode and reference and the glass fiber was employed as the separator. The electrolyte was 1M sodium perchlorate (NaClO$_4$) dissolved in a mixture of propylene carbonate (PC) and ethyl carbonate (EC) (1:1, v/v) with fluoroethylene carbonate (FEC, 10 wt%) as an additive.

Charge-discharge measurements as well as long-cycle life performance were performed between 0.005 and 2.5 V (vs. Na$^+$/Na) by an 8 Channel Battery Analyzer BST-8A (1 mA) from MTI and tested at different current densities. The cyclic voltammetry was conducted with a scan rate of 0.1 mAs$^{-1}$ within a chemical window from 0.005 to 2.5 V (vs. Na$^+$/Na) by a CHI608E electrochemical analyzer. For EIS test, 0.5 mV was applied as the excitation amplitude with a frequency range 10$^{-2}$-10$^5$ Hz.

2.5 Characterization preparation

The morphology of precursor materials, SnO$_2$/C nanoparticles before and after charge and discharge and bare SnO$_2$ particles were observed with SEM and TEM
techniques. The further information about the crystal structure was characterized by Raman spectroscopy technique as well as the XRD with the sample covered on a clean silicon wafer. The silicon wafers were deeply cleaned by the bath sonication for 30 min in the acetone solvent. In order to observe the element distribution in the materials, HRTEM and XPS techniques were used.
CHAPTER III

RESULT AND DISCUSSION

3.1 SEM

Figure 3.1-1 SEM image of precursor materials.

The morphology and microstructure of the sample were characterized by SEM. For the precursor materials in SEM image, prepared by hydrothermal reaction, precursor particles were well dispersed on the holder. (Figure 3.1-1) The precursor materials were
milled into powder and no severe aggregation was found. But no further details about the morphology could be observed due to ultra-small size of the particles. Only rough and unclear powder were found in the SEM image. Most of the surface materials were C ligands as our expected. Even at a higher multiple, the size and the shape could not be detected.

Figure 3.1-2 SEM images of SnO₂/C with different multiples.
After annealing at 500 °C under Ar for 2 h, most of the organic ligands were carbonized and then formed carbon layers. Due to the carbonization, the annealed SnO$_2$/C particles were kind of shrink and the morphology was slightly different from the precursor materials. (Figure 3.1-2) But the annealed materials still remained small size and no further details about the surface could be observed, even in a higher magnification. In SEM images, those particles were more clear and smooth when compared to the precursor materials.

Besides, In addition, bare SnO$_2$ particles were also fabricated by re-annealing the SnO$_2$/C particles in the air in order to eliminate the carbon layers. And bare SnO$_2$ particles showed similar morphology when compared with SnO$_2$/C particles. (Figure 3.1-2) Small, clear bare SnO$_2$ particles were observed in the SEM image. Since these three materials were not well observed in SEM images, further characterization in TEM need to be done.

![SEM images of bare SnO$_2$ particles.](image)
3.2 TEM

Figure 3.2-1 TEM images of precursor materials.
In TEM image (Figure 3.2-1), small particles were observed and size was around 30 nm. The shape of the precursor materials was random rather than specific shape, which confirmed it would be metal organic composites. Also, the surface of the precursor materials was very rough and the edge was not well defined which showed in the higher multiples image. Based on the XRD spectrum of the precursor materials (Figure 3.6-1), it also concluded that there weren’t any framework structure in the materials.

Also, TEM was employed to further characterize the microstructure of the annealed SnO$_2$/C particles. In low magnification TEM image (Figure 3.2-2), aggregations were observed, consisting of several large particles with size around 100 nm. But actually, they were a group of many small SnO$_2$/C particles with size around 10 nm shown in high magnification TEM image. The shapes of these particles are also random but much clearer and smoother than precursor materials. Each one of these particles was SnO$_2$ materials covered with carbon layer materials.

For SnO$_2$/C particles after charge/discharge, materials morphologies were very different from precursor one and SnO$_2$/C one. As shown in TEM image (Figure 3.2-3), some large, bulk flakes were observed. And some small particles dispersed on those flakes. Those bulk flakes were actually carbon black, which could help to improve the conductivity. And these small particles were Sn and little amount SnO$_2$ mixture just based on the alloying mechanism in charge/discharge process.
Figure 3.2-2 TEM images of SnO$_2$/C with different multiples.
Figure 3.2-3 TEM image of SnO$_2$/C after charge/discharge.

3.3 HRTEM and EDAX
Figure 3.3-1 HRTEM image of SnO$_2$/C nanoparticles (scale bar: 5 nm for (b)) reveals that the d-spacing of the SnO$_2$ (110), (101) planes are 0.33 nm and 0.264 nm.

Figure 3.3-2 (a) STEM Z-contrast image and the corresponding elemental EDX mapping images of (b) tin, (c) oxygen, and (d) carbon.

In high resolution TEM image (Figure 3.3-1), it showed several neighboring crystal planes. And two interplanar distances of them were labeled in the image with 0.33 nm and 0.264 nm. And those distances were corresponding to two distinct peaks (110) and (101).
(101) in the XRD pattern. However, carbon layer materials were not observed in the image, which meant that the carbon were amorphous and did not form graphene-like materials. (Figure 3.6) Based on HRTEM image as well as the XRD data, it could be conclude that SnO₂/C particles are crystalline and made into ultra small particles. The elemental maps of tin, oxygen, and carbon (Figure 3b-d), obtained by using energy-dispersive X-ray spectroscopy (EDX) in STEM mode, revealing uniform distribution of Sn and O in the particles. But for the C, the distribution was different from other 2 images due to not homogenously carbonized and over covering on SnO₂ particles.

![Image](image.png)

Figure 3.3-3 (a) TEM image of SnO₂/C after charge/discharge, (b) STEM Z-contrast image and the corresponding elemental EDX mapping images of (c) tin, (d) oxygen.
Energy-dispersive X-ray spectroscopy (EDX) technique was also used to detect elemental distribution in the SnO$_2$/C after charge/discharge at the aim to study the alloy mechanism. As shown in the Figure 3.3-3, the selected area was the studying area. Small particles dispersed on those bulk carbon black flakes. In elemental maps, tin and O elements were observed. The tin element distribution focused on those small particles. On the contrary, O element was very different and distribute every. These two maps implied that SnO$_2$ materials were reduced to metallic Sn and form Na$_2$O. Because carbon layers would help to prevent SnO$_2$ or Sn aggregation, metallic Sn could still remain small particles similar to SnO$_2$/C particles before charge/discharge.

3.4 BET

Figure 3.4-1 (a) N$_2$ adsorption-desorption isotherm and pore size distribution curve (inset) of the precursor, (b) N$_2$ adsorption-desorption isotherm and pore size distribution curve (inset) of the annealed SnO$_2$/C nanoparticles.

N2 adsorption-desorption isotherm was done to measure the surface area (Figure 3.4-1). The value of surface area of precursor materials was 268.6712 m$^2$/g (Figure 3.4-1 (a)). Just based on this data, the precursor materials were proved to be highly porous. For
the SnO$_2$/C particles, the surface area was 116.0408 m$^2$/g which confirmed that the outer carbon materials reduced during the carbonization process (Figure 3.4-1 (a)). Besides, the isotherm curve showed a typical type-IV behavior, showing an obvious hysteresis loop at relative pressure P/P$_0$ around 0.5 to1. And it implied that the annealed SnO$_2$/C particles contained a large number of mesopores, which was one of the requirements of the goal materials$^{30}$.

3.5 TGA

In the thermogravimetric analysis (TGA) data (Figure 3.5-1), the precursor materials and the SnO$_2$/C particles were performed in different atmosphere and processes in order to study the annealing process and the C content. For the precursor materials, materials were performed in nitrogen atmosphere at the aim to validate the annealing point. Besides, isothermal treatment was done at about 105 °C at the aim of eliminate all the water trapped in the material. As observed, a clear plateau could be found around 500 °C which proved that the annealing process did finish at about 500 °C. And the slight drop after 600 °C was the reduction from SnO$_2$ to metallic Sn caused by the carbon.

![Figure 3.5-1 (a) TG curve of SnO$_2$/C precursor heated in the nitrogen at 10 °C min$^{-1}$, (b) TG curve of SnO$_2$/C annealed materials heated in the air at 10 °C min$^{-1}$.](image-url)
For the SnO$_2$/C particles, materials were performed in the air at a heating rate of 10 °C min$^{-1}$. By eliminate the C, the SnO$_2$ content of the annealed materials could be measured. And the SnO$_2$ weight content was determined to be 88 wt% while C content was about 10 wt%.

3.6 XRD

![XRD patterns](image)

Figure 3.6-1 XRD patterns of (a) precursor materials, (b) SnO$_2$/C particles.
Figure 3.6-1 showed the XRD patterns of precursor materials and SnO$_2$/C. From Figure 3.6-1 (a), no sharp peaks were found and only some broad peaks were shown. Those broad peaks indicated that precursor materials were amorphous materials rather than crystalline structure. On the other hand, for Figure 3.6-1 (b), the spectrum displayed different sharp peaks. All these peaks could be assigned to the SnO$_2$ (JCPDS card no. 41-1445). Therefore, those peaks confirmed that the particles were crystalline and SnO$_2$ particles.

3.7 XPS

![XPS Spectra](image)

Figure 3.7-1 XPS survey of SnO$_2$/C particles.
(a)

(b)
Beside the EDAX technique, different elements of Sn, C and O in SnO$_2$/C were detected by the XPS technique as shown in Figure 3.7-1. Also, high resolution XPS survey of different elements were also shown in Figure 3.7-2. As shown in Figure 3.7-2 (b), carbonyl carbon (C=O, 287.6 eV) and carboxyl carbon (O-C=O, 289.0 eV) could be found in the curve which meant C also bond with O in SnO$_2$/C particles. And for the Sn element, Sn$^{4+}$ (486.7 eV) peak was found in the curve (Figure 3.7-2 (c)). It implied that Sn element mainly existed as SnO$_2$. 

Figure 3.7-2 High resolution XPS survey: (a) O1s, (b) C1s, (c) Sn3d.
3.8 Electrochemical performance

Figure 3.8-1 Cyclic voltammogram of SnO₂/C nanoparticles collected at a scan rate 0.1 mV/s within the voltage range of 0.005-2.5 V.

The electrochemical reactions, which happened during charge and discharge process in Sn-based battery system, were evaluated by cyclic voltammetry (CV) under a constant scan rate of 0.1 mV/s within a voltage window of 0.005-2.5 V vs Na/Na⁺. As shown in Figure 3.7-1, there were 2 irreversible reactions happened in the 1ˢᵗ discharge process, the plateau around 1.0V. One was the solid electrolyte interface (SEI) film formation on the anode, which could prevent the reaction between anode material and electrolyte. Another one was the metallic Sn formation:

\[
\text{SnO}_2 + 4\text{Na}^+ + 4e^- \rightarrow \text{Sn} + 2\text{Na}_2\text{O}
\]  

(1)
As shown in reaction (1), SnO2 would first react with Na+ and reduce into metallic Sn. Then, metallic Sn would continue to react with Na+ ions to begin the reversible alloying mechanism. Capacity loss was caused by these two irreversible reactions in the 1st cycle. In the following cycles, two different peaks were observed in the every cycle, which were reversible alloying/dealloying reactions:

\[
\text{Sn} + 3.75\text{Na}^+ + 3.75\text{e}^- \leftrightarrow \text{Na}_{3.75}\text{Sn} \tag{2}
\]

One was observed around 0.5 V in the discharge process, which revealed the two-phase sodiation to form -NaSn and Na\text{9}Sn\text{4}. Another one was around 0.005 V, indicating the single-phase sodiation for further alloy to obtain Na\text{3}Sn and Na\text{15}Sn\text{4}. Meanwhile, there are another two peaks in the charge process, corresponding to single-phase as well as two-phase dealloying process.
Figure 3.8-2 (a) Specific capacities at current density range from 50 mA/g to 2 A/g, (b) Charge/discharge profiles for 1st and 2nd cycles at current density of 50 mA/g and 2nd cycles at a current density of 200 mA/g, 500 mA/g, 1 A/g, 1.5 A/g and 2 A/g.

Furthermore, the rate performance of SnO$_2$/C particles anode was employed with different current density from 50 mA/g to 2A/g (Figure 3.8-2 (a)). The anode material delivered 440 mAh/g at 50 mA/g. Then, when the current density increased to 2A/g, the corresponding capacity could still remain more than 150 mAh/g. Finally, when the current density was decreased to 50 mA/g, the capacity could recover more than 400 mAh/g, which was very to the original value at first 5 cycles. The data showed that SnO$_2$/C particles had good rate capability and was able to tolerant fast Na$^+$ ions diffusion. The corresponding charge/discharge profile was also shown (Figure 3.8-2 (b)). The fast diffusion was because carbon layers could help to improve the conductivity of the Sn-based materials so that electrons could move faster which was important in high rate performance.
Figure 3.8-3 (a) Long cycle performance of SIBs at current density of 1 A/g and 500 mA/g (50 mA/g was used for activation in the first 5 cycles), (b) Charge/discharge profiles for 1st and 2nd cycles at current density of 50 mA/g and 1st and 200th, 500th cycles at a current density of 1 A/g.
Figure 3.8-3(b) showed the long cycle test results. SnO\(_2\)/C anode materials were tested over 500 cycles at high current density 500 mA/g and 1 A/g. And meanwhile, bare SnO\(_2\) anode materials were also tested at 500 mA/g as contrast. For the bare SnO\(_2\) one, capacity faded out quickly in first few cycles. And nearly no capacity was exhibited in following cycles, which was mainly ascribed to the aggregation of SnO\(_2\) particles. On the other hand, for SnO\(_2\)/C particles, performance at both 500 mA/g and 1 A/g were showing good stability. After 500 cycles, the capacity remained 260 mAh/g at 500 mA/g with retention of 78% and 170 mAh/g at 1 A/g with retention of 71%, respectively. The corresponding charge/discharge curves of SnO\(_2\)/C particles at 1 A/g were showed in Figure Figure 3.7-3(a). For these good long cycle performances, carbon layers played an important role in it. Carbon layers not only improved conductivity but also prevent large agglomeration. Also, small size of the active material would also help to shorten ions diffusion pathway and accommodate volume expansion. Because of these 2 reasons, the morphology of SnO\(_2\)/C particles can be very stable when undergoing such high current density charge/discharge process.
Figure 3.8-4 Nyquist plots of SnO$_2$/C electrodes in their pristine state and after 1000 charge/discharge cycles at (a) 500 mA/g and (b) 1A/g.

Besides, Electrochemical Impedance Spectroscopy (EIS) technique was also used to measure the impedance of batteries before and after charge/discharge test in order to study the change of the electrodes. As shown in Figure 3.7-3(a), for the battery at 500 mA/g, impedance was around 3000 ohm before charge/discharge. And the impedance reduced to less than 2000. The reason might be the electrode materials tend to be stable after many charge/discharge cycles. The similar situation happened in the battery at 1A/g, which had around 1700 ohm and 900 ohm before and after 1000 cycles, respectively. In addition, these impedance data were higher than most data from other works might because of glass fiber as separator in batteries.

As shown in SIBs study with the SnO$_2$/C anode, this material was favorable for sodium storage properties. And such electrochemical performances were ascribed to
following properties: (1) the ultra-small sizes of the particles help to shorten the Na\(^+\) ions diffusion pathway as well as accommodate the volume expansion. (2) The carbon layers, which covered on SnO\(_2\) particles, were able to improve the conductivity of SnO\(_2\). Besides, the carbon layers could also prevent aggregation of SnO\(_2\) during the charge/discharge process. (3) The SnO\(_2\)/C particles were highly porous based on the BET data, indicating that the electrolyte were able penetrate through the materials and attach with active materials very well. And all these three reasons could boost and stable the alloying/dealloying mechanism, which finally lead to an outstanding performance. Most importantly, this hydrothermal method was very easy and has just a few steps to fabricate the goal materials. That might be another promising method to prepare suitable anode or cathode materials for both LIBs and SIBs.
CHAPTER IV

CONCLUSION AND PROSPECT

In summary, SnO$_2$/C particles were successfully fabricated by hydrothermal reaction as well as annealing process, and made in ultra-small size. SnO$_2$ particles were covered with porous carbon layers and exhibited good electrochemical performance. These structure properties could mitigate the volume expansion and promote the stability of the structure during charge/discharge process. And SnO$_2$/C anode was employed in SIBs and performed good rate capability. Also, it exhibited high reversible capacity of 160 mAh/g at high current density of 1 A/g. Those results demonstrated that these SnO$_2$/C particles might be an ideal material for sodium-based energy storage system. And this easy synthesis method should be high lined in the particles applications in the energy storage materials.
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