Electrochemical behavior of nanocrystalline tin oxide electrodeposited on a Cu substrate for Li-ion batteries

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Nanocrystalline (5–10 nm) Cu-doped (~3–25 at%) tin oxide films have been obtained by electrochemical deposition on a Cu substrate. In the initial stage of electrodeposition, the Cu$^{2+}$ ions dissolved from the Cu substrate and then co-deposited back with tin oxide on the substrate. The dQ/dV figure for the assembled cell, using the Cu-doped tin oxide as anode, indicated that Li$_2$O possessed electrochemical reversibility in a high voltage range (larger than 1.2 V), and it was maintained for at least 15 charge/discharge cycles. Both the nanometer dimensions of the deposited coating and the Cu doping in the SnO$_2$ lattice activated the Li$_2$O to transform metallic Cu and Sn to metal oxides (CuO and SnO$_2$) and Li$^+$ ions. Thus the capacity of SnO$_2$ coatings can be promoted from the contribution of reactions involving the formation/decomposition of Li$_2$O besides the alloying/dealloying of Sn with Li. The effect of the cutoff voltage range on the capacity and cyclability was also discussed. At voltages lower than 1.0 V, Li$_2$O cannot be activated due to the deficiency of overpotential. The absence of Li$_2$O decomposition during the charging step led to a lower capacity but a stronger binding between the Li$_2$O and other particles. Thus the cyclability for a low maximum voltage (415 mAh g$^{-1}$ at the 15th cycle) was better than that for high maximum voltage. The experiment not only provides a novel, fast and low-cost process to fabricate anodes for Li-ion batteries, but also clarifies the electrochemical behavior of the nanocrystalline Cu-doped SnO$_2$ electrode.

Introduction

In recent years, lithium-ion batteries are becoming the main power sources of rechargeable batteries for portable electronics. They can store more energy per unit volume or weight than nickel–metal hydride, nickel–cadmium and lead–acid batteries. Although graphite is available commercially as an anode material for Li-ion batteries, the research of high-performance materials is still an active area.

Tin oxide is one of the potential anode materials for Li-ion batteries because of the high capacity, which is more than twice that of graphite. For the conventional electrochemical characterization of SnO$_2$, the reaction can be distinguished as reversible and irreversible reactions. The irreversible one is described as follows.\cite{1,2}

\[ 4\text{Li}^+ + 4\text{e}^- + \text{SnO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{Sn} \] (1)

Most of the Li$_2$O is formed in the first cycle and only little Li$_2$O can be recycled in the following cycles as the particle size of the electrode is in the micrometer-scale range. The reversible reaction, which is described below, is the alloying/dealloying of Sn with Li:\cite{2}

\[ \text{Li}^+ + \text{e}^- + \text{Sn} \leftrightarrow \text{LiSn} \] (2)

\[ 3.4\text{Li}^+ + 3.4\text{e}^- + \text{LiSn} \leftrightarrow \text{Li}_4\text{Sn} \] (3)

The alloying and dealloying reactions result in the formation of cracks due to the volume change during the charge/discharge steps.\cite{3,4} The volume change destroys the structure of the electrode material and consequently damages the cyclability in the following cycles. The methods for cyclability enhancement of tin oxide include doping other metals into the SnO$_2$ structure,\cite{5} amorphization\cite{6,7} and addition of other oxides.\cite{8,9} Theoretically, nano-sized particle materials also can enhance the cyclability of the reversible reaction due to the minimization of Sn clusters and the increased reaction area. However, the capacity is usually poorer than expected or the electrochemical behavior is hard to measure, especially when the raw materials are processed in the powder form. The reason is the difficulty of well dispersing the nano-sized particles with the binder and carbon black during the scraping process, and thus the smaller particle size often leads to a lower capacity and/or a poor cyclability. In the consideration of the interference of dispersing nano-sized particles, it is difficult to fully characterize the real effects of nano-sized materials for Li-ion batteries.

Nanocrystalline SnO$_2$ has been synthesized successfully by electrochemical deposition in nitric acid solution on a copper plate.\cite{10} In the nitric acid solution, OH$^-$ ions were formed on the cathode by the reaction that follows,

\[ \text{NO}_3^- + 2\text{e}^- + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + 2\text{OH}^- \] (4)

In our preliminary studies, it was found that the stannic ions and hydroxo complexes of Sn(iv) react with OH$^-$ ions to precipitate an underlying dense layer and an upper porous layer on the cathodic surface, which provided both good adhesion and large surface area respectively. The porous layer offers large surface area and void space for Li$^+$ ions to react and diffuse during the charge and discharge steps. Thus electrodeposited SnO$_2$ is a good choice of anodic material for Li-ion batteries, and we can characterize the actual effects of nano-sized SnO$_2$ particles without the interference of the dispersion problem. Because the precipitation characteristics of SnO$_2$ particles are very sensitive to both the stannic ion concentration of the solution and the current density of electrodeposition, the experimental parameters have to be strictly controlled in order to obtain the upper porous layer.

The paper describes the characteristics of nano-sized SnO$_2$ coatings deposited by electrodeposition in nitric acid solution on Cu substrates and the consequent electrochemical behavior of the coatings as anode materials for Li-ion batteries. The
differential capacity diagrams were used to analyze the electrochemical behavior of coatings and to discuss the effects of nano-sized particles on anode performance for Li-ion batteries.

**Experimental**

The solution was composed of 25 mM SnCl₂·2H₂O (Riedel-de Haén, 99.8%) and 150 mM HNO₃ (J.T. Backer, A.C.S. reagent) balanced by redistilled water. The solution was maintained at 85 °C in the duration of solution pre-treatment and during electrodeposition. For the pre-treatment step, oxygen was blown into the solution for one hour at a flow rate of 100 sccm (standard cubic centimeter per minute) in order to oxidize the stannous ions into stannic ones. Then the solution was poured into an electrochemical cell, and the electrodeposition was performed as soon as possible.

A copper disk (Alfa Aesar, 99.99%) of 14 mm diameter was used as the working electrode, which was cleaned sequentially with acetone and diluted hydrochloric acid solution before deposition. The cell for deposition was a two-electrode cell, in which a Pt metal plate was used as the counter electrode with a separation from the working electrode of 25 mm. An O-ring with a diameter of 10 mm was used to seal the working plate during the deposition. Oxides were deposited using an EG&G potentiostat (Model 263A) at a current density of 10 mA cm⁻² for 150 s to obtain a porous film with a thickness of about 0.8 μm. The deposits were washed with deionized water several times to remove the remaining chloride contaminant and then dried under ambient conditions. As measured by a high-precision electronic balance, the weight gain of coatings was within the range of 0.28 to 0.34 mg cm⁻².

The phase and related element distribution of the films were analyzed by XRD and Auger electron spectral analysis respectively. Grain size and microstructure were observed by TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope. After scraping the coating into ethanol, a drop of suspension was deposited onto a TEM on a Philips XL-40FEG microscope.

**Results and discussion**

**Characterization of tin oxide coating**

A SEM image of the as-deposited tin oxide (Fig. 1a) shows the microstructure of the coating, which was composed of particles with size of about 50 to 100 nm. In fact, these particles were composed of a large amount of extremely fine crystallites, which will be discussed later. The highly porous coating had a large surface area preferred for the applications of Li-ion batteries. Fig. 1(b) shows a bright field image and the diffraction ring of the as-deposited coating. The bright field image indicated that the nano-sized particles ranging from 5 to 10 nm aggregate into a larger particle, as observed by SEM in Fig. 1(a). The diffraction ring was over-exposed in order to confirm whether other impurity precipitates were present, and the result was double-checked. The diffraction ring can be characterized as the tetragonal tin oxide phase without the presence of other impurities in the SnO₂ coating. The low-angle X-ray pattern of the as-deposited coating (not shown here) also demonstrated the same result. The chemical composition analysis from EDS in TEM shows that the Cu content in SnO₂ is within the range of 3 to 25 atomic percent. According to the pure diffraction rings, the precipitation of Cu, CuO or Cu₂O was excluded and the presence of Cu in the form of Cu(II) doped in SnO₂ was the most reasonable condition. The Cu content was unexpectedly high compared with that prepared by other processes,¹²,¹³ and the result will be discussed briefly later. The ionic radii of Cu²⁺ and Sn⁴⁺ ions were very close (0.073 and 0.069 nm respectively), so the determination of Cu concentration from the radius variation of the diffraction ring was very difficult. Due to the large difference of the Cu content at different positions, further analysis was needed to determine the distribution of Cu. Based on the low process temperature, Cu doping in SnO₂ can be attributed to the dissolution of the Cu substrate during deposition rather than the diffusion from the Cu substrate into the deposited SnO₂ nano-particles. During deposition, the dissolution of Cu²⁺ ions only lasted for several seconds, because it was terminated as the SnO₂ coating covered the whole surface of the Cu substrate. The continuous coating stopped the supply of Cu²⁺ ions dissolving into the solution from the substrate and led to the decrease of Cu²⁺ ions near the cathode. Consequently, the Cu concentration near the
interface of Cu and SnO$_2$ was much higher than that near the coating surface. The distribution of Sn and Cu from Auger analysis is shown in Fig. 2, which demonstrates the results mentioned above. The Cu concentration at the inner part of the coating maintained at about 25 atom% and that at the outer part decreased gradually. The real distribution of Cu at the interface was expected to be sharper because the measured result was disturbed by the roughness of the Cu substrate.

Electrochemical behavior for Li-ion batteries

Fig. 3 shows the differential capacity vs. voltage for SnO$_2$ deposited on Cu and Pt substrates for 150 seconds with the Pt substrate being used as the reference material. Fig. 3(a) shows the electrochemical behavior of Cu-doped SnO$_2$ coatings during charge/discharge testing. In the first discharge step, similar to the ordinary SnO$_2$ electrode prepared by other processes, Li$_2$O was synthesized (denoted as reaction (a) and described by equation (1)) in the high voltage range (larger than 1 V). It must be noticed that the decomposition of Li$_2$O$^{14}$ (reaction (b)) took place in the following charge steps and was maintained at least to the 15th cycle. The reaction voltages of Li$_2$O for both formation and decomposition shifted toward the more positive values with the cycle number. It is interesting to find that the “irreversible” Li$_2$O became reversible for the Cu-doped and nano-crystalline SnO$_2$ coating. Although the decomposition/formation of Li$_2$O declined gradually with cycle numbers, they still provided considerable capacity besides the alloying/dealloying of Sn with Li. The electrochemical reversibility of Li$_2$O can be attributed to the Cu doping and/or the nanometer dimensions of particles, which will be clarified later. Fig. 3(b) shows the differential capacity vs. voltage for SnO$_2$ deposited on the Pt substrate. The SnO$_2$ coating deposited on the Pt substrate definitely did not contain Cu, while other characteristics, such as particle size and crystallinity, were found to be very similar to those for SnO$_2$ deposited on the Cu substrate. Considering that the Pt dissolves at around 0.2 V vs. Li/Li$^+$, the voltage range for examination was limited to between 0.5 V to 2.5 V, and the un-doped SnO$_2$ coating also exhibited the characteristic electrochemical reversibility of Li$_2$O at least to the 15th cycle. Poizot et al. conducted a study on the electrochemical properties of several transition metal oxides, such as FeO, MoO, NiO, CuO and so on, for cathode materials of Li-ion batteries. Their research revealed the electrochemical reversibility of Li$_2$O. They believed that the nano-sized metal particles (10 to 20 nm) formed during discharge could activate the nanocrystalline Li$_2$O and promoted its electrochemical reversibility because of the large surface area of the nano-sized metal particles. For the raw materials in micro-sized dimensions, metallic Sn particles larger than 30 nm$^{16,17}$ have been demonstrated to be unable to activate Li$_2$O for electrochemical reversibility. It can be expected that SnO$_2$ particles smaller than 10 nm can lead to the formation of Sn particles with the same or even smaller size, which in turn can activate the transformation of Li$_2$O into Li$^+$ ion during discharge steps. Thus, the nano-sized particles of Cu-doped SnO$_2$ provided at least a partial contribution to the electrochemical reversibility of Li$_2$O.

So far as the electrochemical behavior for Li-ion batteries is concerned, the ass-deposited Cu-doped SnO$_2$ can be regarded as a mixture of CuO and SnO$_2$ during the charge/discharge steps, which will be discussed later. On the aspect of transition metal oxides for Li-ion batteries, the Cu(II) in the SnO$_2$ structure may also improve the electrochemical reversibility of Li$_2$O, similar to the conclusion suggested by Poizot et al. In our study on the electrodeposition of tin oxide, it was found that the dissolved Cu$^{2+}$ was consumed gradually during deposition, and then the Cu concentration in the coating significantly decreased due to a drastic precipitation of SnO$_2$ particles after about 130 seconds of deposition. Therefore, the surface and average Cu concentrations of the coating prepared for 300 seconds were expected to be much less than those for the coating prepared for 150 seconds. The difference can be used to realize the effect of Cu doping on the electrochemical behavior. Fig. 4 shows the Li$_2$O capacity contributions of the Cu-doped SnO$_2$ deposited for 150 and 300 seconds respectively. The capacity contribution of Li$_2$O was calculated from the peak area under the peak of Li$_2$O decomposition to the area of whole voltage range in the
In the higher voltage range (1.2–2.0 V), Li$_2$O is activated by nanocrystalline Sn particles $^{2}$ and Cu particles $^{300}$ seconds. $^{2}$ denotes the ratio of Cu to Sn in SnO$_2$ lattice, which is between $x$. The growth of tin particles reduced the activity of tin particles for Li$_2$O. Thus the capacity contribution of Li$_2$O declined with cycle number, which also can be observed in Fig. 4. Moreover, it was not easy to precisely control the duration of Cu dissolution during electrodeposition, but the Cu concentration in the as-deposited coating and the capacity contribution of Li$_2$O were found to be similar for different runs of coatings deposited for 150 seconds, demonstrating the good reproducibility of the process.

In this paragraph, the electrochemical behavior of nanocrystalline Cu-doped SnO$_2$ for Li-ion batteries in both the charge and discharge steps will be described step by step. During discharge, Li$_2$O, nano-sized Sn and Cu are formed in the voltage range above 1 V.

Sn$_{1-x}$Cu$_x$O$_{2-x}$ + (4 - 2$x$)Li$^+$ + (4 - 2$x$)e$^{-} \rightarrow (1 - x)$Sn + $x$Cu + (2 - $x$)Li$_2$O  \hspace{1cm} (5)

$x$ denotes the ratio of Cu to Sn in SnO$_2$ lattice, which is between 0.03 to 0.25 from the chemical composition analysis. The Li-Sn alloy is formed within the voltage range below 0.6 V.$^2$ as described by the following reaction.

4.4Li$^+$ + Sn + 4.4e$^{-} \rightarrow Li_{4.4}Sn$  \hspace{1cm} (6)

The reaction described above is the total reaction of equations (2) and (3). During the charge step, the Li$_{4.4}$Sn is oxidized in the low voltage range (0.1–0.7 V)$^2$

Li$_{4.4}$Sn $\rightarrow$ 3.4Li$^+$ + LiSn + 3.4e$^{-}$  \hspace{1cm} (7)

In the high voltage range (0.8–1.3 V), LiSn is deaolloyed into nanocrystalline Sn particles$^3$

LiSn $\rightarrow$ Li$^+$ + Sn + e$^{-}$  \hspace{1cm} (8)

In the higher voltage range (1.2–2.0 V), Li$_2$O is activated by highly active Sn and Cu particles to form Li ions and the respective oxides SnO$_2$ and CuO. However, during TEM characterization of the products (not shown here), only the diffraction pattern of SnO$_2$ is observed, but the EDS analysis still confirms the presence of Cu. The absence of a diffraction pattern for copper oxide is expected to be due to the formation of the amorphous phase of copper oxide. Because the formation voltages and formation mechanisms of these two metal oxides are different, we believe that the composite of tin oxide and copper oxide is the product after charge.

3Li$_2$O + Cu + Sn $\rightarrow$ CuO + SnO$_2$ + 6Li$^+$ + 6e$^{-}$  \hspace{1cm} (9)

In subsequent cycles, copper oxide and tin oxide re-decomposed during discharge and then re-formed during charge.

The redox reaction involved the decomposition/formation of Li$_2$O, activated by the nanometer dimensions of the component and/or Cu doping, which in turn promoted the capacity of SnO$_2$. Thus a high capacity of the nano-sized and Cu-doped SnO$_2$ anode can be predicted. The other important property, the cyclability, directly affected by the cutoff voltage range will be discussed in the following paragraph.

The effect of cutoff voltage range

Fig. 5 shows the differential capacity vs. voltage diagram of Cu-doped SnO$_2$ deposited for 150 seconds at the maximum voltage of 1.5 V vs. Li/Li$^+$. The electrochemical behavior in the first cycle was similar to that for the maximum voltage of 2.5 V, while the reaction peaks for the formation/ decomposition of Li$_2$O in the following cycles were smaller. The lower maximum voltage led to a lower capacity from Li$_2$O due to the smaller overpotential. Only a small amount of Li$_2$O formation and decomposition for the voltage range from 1.0–1.5 V was found. Thus the maximum voltage should be as high as possible to increase the capacity from the contribution of the formation/ decomposition of Li$_2$O. However, many researchers indicated that both high voltage and low voltage conditions should be avoided to obtain better cyclability.$^4,5,16,19$ It is reasonable to argue that there should be an appropriate voltage range to provide a better combination of adequate capacity and cyclability.

It can be expected that the wide cutoff voltage range led to a high capacity due to the contribution of Li$_2$O in the several initial cycles, but the behavior of rapid capacity decay during the subsequent cycles should be noticed. Fig. 6 shows the diagram for discharge capacity vs. cycle number for different maximum voltages from 2.5 V to 1.0 V vs. Li/Li$^+$. The higher maximum voltage leads to a higher capacity in several initial cycles but with poorer cyclability. The ultra high capacity for the first cycle can be attributed to the hydroxyl bond in the as-deposited coating. During the discharge step of the first cycle, one Sn(OH)$_4$ (tin hydroxide) leads to the formation of
four Li$_2$O molecules rather than two on the anode. For the initial eight cycles, the capacity for the cutoff range from 2.5 V to 0.05 V is larger than 1000 mAh g$^{-1}$, which is extremely high compared with most micro-sized tin oxides. The unexpected high capacity was due to the reaction involving the decomposition of Li$_2$O. After 15 cycles, the discharge capacity decreased to 647 mAh g$^{-1}$, which was still about twice that of using graphite as the anode materials. The case of 1.5 V–0.05 V showed lower capacity in several initial cycles but better cyclability in the subsequent cycles. The better cycle retention can be attributed to reduced decomposition of Li$_2$O. It was reported that lithium oxide has a glue function that can adhere other particles within a matrix to the substrate as it is formed during the discharge step. If Li$_2$O becomes an active material, the decomposition of Li$_2$O during the charge step will weaken the adhesion between the Li$_2$O matrix and other particles, and even cause the formation of cracks. Thus the capacity declined with the decomposition of Li$_2$O during the charge steps. It was reported that the reason why the cutoff voltage range of 1.0–0.05 V has the best cyclability is due to the absence of Li$_2$O decomposition and Sn atom aggregation. The higher contribution of the low-voltage-range part of the discharge capacity for the test of high maximum voltage range can be compared in Figs. 3(a) and 5. Comparing with other processes for the fabrication of electrode for Li-ion batteries, electrodeposition of tin oxide is a relatively fast, low-cost, and low-temperature process. Besides, the one-step processing, free from the procedures of scraping, further promotes the reproducibility and reliability of the electrochemical properties of SnO$_2$ for Li-ion batteries. The advantages of simpler procedure and superior performance of coatings lead to an enormous potential for SnO$_2$ as an anode material for Li-ion batteries. Moreover, in previous reported research, the presence of the phenomenon of decomposition/formation of Li$_2$O limits its use to reactions involving some transition metal oxides. According to the results in this paper, other nano-sized metal oxides, like SnO$_2$, also can activate the reaction even if the electrodes are free from binder and carbon black.

**Conclusion**

Nano-crystalline Cu-doped tin oxide can be obtained by electrodeposition in nitric acid solution on the Cu substrate. The highly porous morphology and nano-sized particles are above, we can conclude that the inferior cyclability for the maximum voltage of 2.5 V, compared to that of 1.5 V, was due to the increased decomposition of Li$_2$O. The best cyclability of 1.0 V, compared to those of 1.5 V and 2.5 V, was due to the absence of decomposition of Li$_2$O and Sn aggregation.

For the present study the case for the voltage range of 1.0 V to 0.05 V possesses good cyclability for the as-prepared tin oxide for anode materials of Li-ion batteries. Though the electrochemical properties, e.g., the capacity and cyclability, of the electrodeposited tin oxide are far better than those of the as-prepared un-doped tin oxide by conventional wet chemical methods. However, compared with the conventionally prepared samples after heat treatment, the electrochemical properties of the electrodeposited tin oxide are not particularly outstanding. It was reported that heat treatment of tin oxide can substantially promote the cyclability and capacity; therefore, it is expected that the electrochemical properties of the electrodeposited tin oxide can be further promoted via post-deposition heat treatments. Besides, the difference in capacity for maximum voltages of 2.5 V and 1.0 V cannot be totally regarded as the capacity contribution of the reaction involving Li$_2$O decomposition. The high voltage also affects the behavior of alloying/de-alloying of Sn–Li alloy, which is classified as the low-voltage-range reaction. Thus, the difference of capacity for the two cases can be attributed to both the reactions involving Li$_2$O and Sn–Li alloy. The higher contribution of the low-voltage-range part of the discharge capacity for the test of high maximum voltage range can be compared in Figs. 3(a) and 5.
suitable for the anode materials for Li-ion batteries. Both Cu doping and nanometer dimensions of SnO$_2$ can increase the electrochemical reversibility of Li$_2$O that is irreversible for the case of using micro-sized SnO$_2$. The capacity is further promoted from the reaction involving formation/decomposition of Li$_2$O besides the alloying/dealloying of Sn with Li. Meanwhile, the decomposition of Li$_2$O during the charge step also weakened the adhesive bonding between the Li$_2$O matrix and other particles. Consequently, a higher maximum voltage led to a poorer cyclability. For the cutoff voltage range from 2.5 to 0.05 V, the highest capacity (about 1250 mAh g$^{-1}$) was obtained in the early stage of cycling, but it also had the poorest cyclability. The low maximum voltage (1.0 V) led to a low capacity (above 400 mAh g$^{-1}$), while the cyclability was superior to that for other cutoff voltage ranges.

In summary, a novel, fast, low-temperature and low-cost process to fabricate high-performance anodes of Li-ion batteries is presented and discussed. Nano-sized and Cu-doped SnO$_2$ has enormous potential because of the reaction involving the redox of Li$_2$O and a consequent high capacity. The effects of the nanocrystalline nature and Cu doping on the electrochemical behavior of electrodeposited tin oxide coatings are also clarified in the present study.

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