Performance of Sn-based Negative Electrode Films Prepared by Electrostatic Spray Deposition in Lithium Batteries

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ABSTRACT

SnO₂ and CuSnO₂ were successfully sprayed onto a Ni substrate using electrostatic spray deposition to produce negative electrode films with highly porous morphologies for use in lithium batteries. The spray-deposited SnCl₂ decomposed to Sn during heat treatment at 230°C under inert atmosphere and then was oxidized to SnO₂ being exposed to the air. The resultant SnO₂ film, which did not contain any additives such as binders or conductive additives, was used as a negative electrode. At the beginning of some charge-discharge cycles, the SnO₂ film achieved a capacity of 780 mAh g⁻¹, which was close to its theoretical capacity. However, its capacity subsequently decreased because of crystal growth during the Li alloying-dealloying process. The capacity retention of the film was improved by adding Cu to the precursor solution. Although the initial capacity of the CuSnO₂ film was lower than that of the SnO₂ film, the CuSnO₂ film displayed better cycle performance; i.e., it possessed more than double the capacity of the SnO₂ film after 100 cycles.

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1. Introduction

High performance power sources are required for mobile electronics, power tools, electric vehicles, etc. Lithium ion batteries are promising potential energy sources for such appliances. Recently, high capacity lithium ion batteries, such as the Nexelion® (SONY), which partially employs a metal alloy as a negative electrode, have come onto the market. However, the metal alloys in these batteries have to be treated with other materials such as carbon to counteract the volume changes induced by Li alloying-dealloying.

Thus, various groups have attempted to develop negative electrodes for lithium batteries made of metals or other compounds that can form alloys with lithium, such as Sn, Si, Sb, etc.^{1,2} Sn and SnO₂ are promising materials due to their low voltage and high capacity (781 mAh g⁻¹).³ The primary problem with metal negative electrodes is their poor cycle performance. The cycle life of Li batteries containing metal negative electrodes is limited by the exfoliation of the electrode due to volume changes during the Li alloying-dealloying process. Cycle performance can be improved by using nano-sized materials,⁴ a roughed substrate, or dispersed particles in the electrode; producing electrodes composed of a thin film of material;⁵ or by adding a third element such as cobalt,⁶ nickel,⁷ iron,⁸ etc. to the electrode. However, none of these methods have been able to achieve good cycle performance and high capacity simultaneously.

Electrostatic spray deposition (ESD) is a unique method of film formation, which was initially developed by Schoonman et al. for use in the battery field.⁹ ESD makes it possible to produce positive electrode films and to vary the deposition conditions, allowing the creation of dense or porous films with pore size and/or wall thickness values ranging from less than one micrometer to over ten micrometers.^{10–12}

In this study, Sn and SnCu films without any binders or conductive additives were prepared using ESD, and the surface morphologies and electrochemical properties of the films were investigated.

2. Experimental

Sn and CuSn films were prepared by liquid-delivered ESD with a downward spraying setup.¹³ Tin chloride (SnCl₂) (Wako Pure Chemical Industries, Ltd.) was dissolved in ethyl alcohol at a concentration of 0.005 mol dm⁻³ as a precursor solution for the Sn film. The CuSn precursor solution consisted of ethyl alcohol containing 0.003 mol dm⁻³ of copper chloride (CuCl₂) and 0.0025 mol dm⁻³ of SnCl₂. These precursor solutions were sprayed from a nozzle at a rate of 0.5 ml h⁻¹. The nozzle was placed 15 mm from the Ni substrate. A positive high voltage (3–5 kV) was applied between the nozzle and the substrate, and the solutions were sprayed in cone-jet mode.¹⁴ The precursor solutions were atomized at the end of nozzle before being delivered onto the substrate. The substrate was heated at 80, 100, 140, or 220°C to produce different surface morphologies and then annealed at 230°C 2 h under an Ar stream to induce thermal decomposition of the precursor solution. The films that formed on the substrate were ca. 3 µm thick.

The surface morphologies and elemental compositions of the films were investigated by scanning electron microscopy (SEM; JSM-6700F, JEOL Ltd.) with energy dispersive X-ray analysis (EDX; Genesis XM2, EDAX). The crystal structure of each film was identified by X-ray diffraction (XRD; RINT 2000, Rigaku Corp.).

The electrochemical performance of the films was tested using charge-discharge tests, which were performed without any additives such as conductive materials or binders. Coin-type cells were assembled in an argon filled glovebox (Miwa Mfg. Co., Ltd.) using Celgard 2400 as a separator, 1 mol dm⁻³ of LiPF₆ in ethylene carbonate and diethyl carbonate (1:1 v/v) as an electrolyte (Tomiya Pure Chemical Industries, Ltd.), and lithium metal foil (Honjo Metal Co.) as a counter electrode. The charge-discharge experiments were carried out using a computer-controlled potentiostat (BS-2500, Keisokuki Center Co., Ltd.) with a current density of 200 mA g⁻¹ and a voltage range of 0.005 to 1.5 V.

Figure 1. Scanning electron micrographs of the Sn based films prepared by ESD at various temperatures; i.e., (a) 80°C, (b) 100°C, (c) 140°C, and (d) 220°C.

3. Results and Discussion

The surface morphologies produced by the ESD of SnCl_2 onto Ni substrates that had been heated at various temperatures are shown in Fig. 1. All of the films were heated at 230°C for 2 h in an inert atmosphere after their deposition. A flat surface was obtained by heating the Ni substrate at low temperature [80°C, Fig. 1(a)]. As the temperature of the Ni substrate was increased, the film became more porous, producing a cobblestone-like morphology [100°C, Fig. 1(b)], followed by a surface containing many rough raised regions surrounded by shallow channels [140°C, Fig. 1(c)]. When the substrate was heated further, these raised regions formed pillars, became more aggregated, and were surrounded by deeper channels [220°C, Fig. 1(d)]. We previously reported that the surface morphologies of lithium oxide compounds used to produce positive electrodes can be controlled by managing the evaporation of the precursor solvent; i.e., by adjusting the deposition temperature,^{11,12} and other metal compounds can also be controlled in this manner to produce various surface morphologies.¹⁵

The XRD profile of the Sn film, which was obtained after it had been annealed at 230°C, is shown in Fig. 2. Its XRD pattern agrees with that of SnO_2 . The annealing temperature was the same as the decomposition temperature of SnCl_2 , which was measured by thermogravimetric/differential thermal analysis (data not shown). In addition, Sn crystals are small and have a large surface area and so are easily oxidized by air.¹⁶

We did not try to increase the annealing temperature used to induce Sn crystallization in order to avoid oxidation, as this would have caused the Sn to melt (the melting point of Sn is 231.93°C).

Table 1 shows the atomic ratios of the source material, the Sn film prepared using a Ni substrate heated at 220°C, and the same Sn film after it had been heat treated at 230°C for 2 h. The ratios were obtained using EDX. The atomic ratio of Cl/Sn for SnCl_2 agreed well with the theoretical value, 2. The Cl/Sn ratio of as splayed film was 0.8, which means that ca. 60% of the Cl evaporated during the deposition process. Most of the remaining Cl was removed by the heat treatment but ca. 10% of the Sn remained as SnCl_2 , and the residual Cl could not be removed by prolonged heat treatment. A large amount of O was observed before and after the film was heat treated. In 2 dimensional mapping, O, Sn, and Cl were often found in the same locations on the Ni substrate (not shown). Some of the O corresponded to SnO_2 , which was supported by the XRD result.

Figure 2. XRD profile of the Sn based film after heat treatment at 230°C for 2 h (a) and the JCPDS data of SnO_2 (b).

Table 1. EDX results for the Sn based film prepared by ESD and the Sn source.

Component	Sn [at %]	Cl [at %]	O [at %]
SnCl_2	34.3	65.7	—
Sn film before heat treatment	25.8	21.7	52.5
Sn film after heat treatment	28.1	6.1	65.8

Some of the remaining O would have been bound to Cl or other compounds such as solvent-derived compounds.

The voltage profiles of the Sn film during the first 3 cycles at a current density of 200 mA g^{-1} , and its specific discharge capacity and Coulombic efficiency during each cycle are shown in Figs. 3 and 4, respectively. The capacity of the 1st discharge, which was the 1st Li dealloying process, was 780 mAh g^{-1} , being close to the theoretical value. The discharge capacity of the film gradually decreased cycle by cycle. Its Coulombic efficiency peaked at 96% after the 3rd cycle and then continuously decreased to 94% by the 100th cycle, when its discharge capacity was only 136 mAh g^{-1} . Alloying-dealloying is accompanied by changes in the volume of the film particles. Every charge enlarges the surface area of the film due to the growing alloy particles on its surface. During discharge, the particles shrink, which causes some of the Sn to be electrically isolated by the new surface film particles, resulting in cycle-by-cycle decreases in Coulombic efficiency.

Figure 5 shows differential capacity plots derived from voltage profiles, which were produced as a means of investigating the electrochemical behavior of the SnO_2 film during the Li alloying-dealloying process. SnO_2 was reduced to lithium oxide and metallic Sn at 0.85 V during the 1st charge, as described in the following reaction Eq. (1).⁵

However, although the film displayed a slight peak in this voltage region a further cathodic peak was observed at 1.16 V during the first charge. Pure SnO_2 does not react at this voltage, but it was

Figure 3. Voltage profiles of the SnO₂ film during the 1st to 3rd cycles at a current density of 200 mA g⁻¹.

Figure 4. Discharge capacity and Coulombic efficiency of the SnO₂ film as a function of cycle number at a current density of 200 mA g⁻¹.

previously demonstrated that the electrolyte can decompose at this voltage if it contains acetylene black.¹⁷ However, the SnO₂ film displayed almost no carbon signal on EDX, so the irreversible reduction observed at 1.16 V might have involved the residual Cl or some other compounds in the film.

The Li_xSn alloy formation that occurs during charging is described in the following reaction Eq. (2).

Here, the Li_xSn alloys include LiSn, Li₇Sn₃, Li₅, Sn₂, Li₁₃Sn₅, Li₇Sn₂, and Li₂₂Sn₅.¹⁸ It is not clear which redox couples correspond to the various Li_xSn alloy formation peaks observed in Fig. 5. The differential capacity profile of our film displays similar features to a cyclic voltammogram of a thin SnO₂ film prepared by chemical vapor deposition (CVD).⁵ The reaction involving the reversible redox couple a/a', which represented an alloying-dealloying process, became weaker with each cycle. On the other hand, the reactions involving the redox couples b/b', c/c', and d/d' became stronger until the 10th cycle [Fig. 5(a)] and then became weaker [Fig. 5(b)]. Before alloying, the SnO₂ particles in the film are very fine (probably a few nm in diameter) or close to amorphous, as shown by their weak and broad XRD peaks (Fig. 2). The first 3 cycles displayed much simpler differential capacity curves, which only involved a/a', and the film maintained a high capacity during this period. During subsequent cycles, new redox couples; i.e., b/b', c/c', and d/d', appeared, and the capacity of the film rapidly decreased. These new redox couples were previously detected in an SnO₂ electrode that had been heat treated at high temperature (1000°C). Large crystals (ca. 100 nm) grew on the electrode during

Figure 5. Differential capacity plots of the SnO₂ film up to the 10th cycle (a) and for subsequent cycles (b).

Figure 6. Discharge capacity and Coulombic efficiency of the CuSnO₂ film as a function of cycle number at a current density of 200 mA g⁻¹.

the alloying-dealloying process, resulting in poor cycle performance.⁴ In our case, our film consisted of SnO₂ alone without any binders or conductive additives, and Sn crystals would have grown on the film and become bound to their neighboring particles during the alloying process.

A CuSn film was prepared using the same method as was employed for the Sn film. The annealed film contained Cu, Sn, O, and a small amount of Cl. The atomic ratio of Cu to Sn corresponded to Cu₆Sn₅, according to EDX. The specific discharge capacity and the Coulombic efficiency of the film at a current density of 200 mA g⁻¹, and differential capacity plots derived from its voltage profiles are shown in Figs. 6 and 7, respectively. During the 1st cycle, the CuSn film displayed quite poor Coulombic

Figure 7. Differential capacity plots of the CuSnO₂ film during the 1st and 2nd cycles (a) and subsequent cycles (b).

efficiency, which then gradually increased to 97% by the 100th cycle. The discharge capacity of the CuSn film was relatively low compared with that of the Sn film during the early cycles, but had overtaken that of the Sn film by the 40th cycle and was 312 mAh g⁻¹ at the 100th cycle, which was over 2 times greater than that of the Sn film. According to differential capacity plots derived from its voltage profiles, during the 1st cycle irreversible reactions occurred at 1.16 V, as was seen for the Sn film, and around 0.7 V. The irreversible reaction observed at around 0.7 V probably involved Cu or CuSn because no such reaction was seen in the Sn film, but we do not have any evidence to confirm this or the mechanism involved. Subsequent cycles displayed reversible

reactions that decreased in strength on a cycle-by-cycle basis without any new reactions, such as crystal growing, which probably explains the better cycle performance of the CuSn film compared with the Sn film. Previous studies have found that adding Cu improved the reversible cycling behavior of pure Sn electrodes,^{19,20} and we have demonstrated that CuSnO₂ displays better cycling behavior than SnO₂.

4. Conclusions

SnO₂ and CuSnO₂ films without any binders or conductive additives were successfully prepared using a direct and simple deposition method, ESD. The capacity of the SnO₂ film was close to its theoretical value during the first few cycles and then rapidly decreased due to crystal growth during the Li alloying-dealloying process. The cycling performance of SnO₂ can be improved by adding Cu.

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