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Preparation of SnO₂-B₂O₃-P₂O₅ for the anode of Li-ion batteries by aerosol flame deposition(AFD)

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Tin oxide and amorphous tin borophosphate oxide have recently received significant attention as a possible new negative electrode material for lithium ion batteries. We employ a completely new method, called "Aerosol Flame Deposition (AFD)", to synthesize the amorphous tin oxide anode for a lithium ion secondary battery. In the deposition process, single or multi-component amorphous oxide nano particles (soot) were synthesized by supplying metal halide sources such as chloride in the form of a gas into an oxy-hydrogen flame. The deposited soot composed of synthesized nano particles was subsequently consolidated by a high temperature heat treatment. The fine powder obtained was a mixture of crystalline tin oxide and an amorphous phase of B_2O_3 and P_2O_5 , resulting in a highly dispersed structure with nano-scale interfaces. The mixture was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). According to the XRD results, the as-prepared materials seemed to have a semi-amorphous structure. However, SEM images showed that the tin-oxide was of a nano-crystalline structure with an average particle size of < 50 nm. The heat treatment improved the crystallinity of the tin oxide significantly. SEM images of the deposited surface after sintering revealed that the deposited soot was converted from a glass structure into amorphous borophosphate oxide and nano-crystalline tin oxide grains. The nano-structured SnO₂-based electrode obtained exhibited improved capacity and cycling stability when tested in a conventional coin type cell.

Key words: SnO₂-B₂O₃-P₂O₅, Tin oxide, Aerosol Flame Deposition, Li-ion batteries, Anode.

Introduction

Rechargeable Li-ion secondary batteries have various applications in electronic devices such as micro-electromechanical systems, smart cards, and medical appliances. To realize Li-ion batteries, each part of the battery cell must be developed to a practical level of performance. Among the components of batteries, the anode is less developed compared to the cathode and electrolyte. In addition, a large number of materials have been investigated application in lithium-ion batteries.

Several materials have been discussed as candidates of the anode such as Li metal, carbon, Si and tin oxide. Due to the intense reactivity in air, Li metal is unlikely to become a popular anode material. Therefore, the practical materials for anode seem to be limited to a metallic alloy of Si, amorphous oxides containing SnO, and some oxynitrides. Among these material systems, the SnO₂ system was selected as an anode in this study. Tin oxide is very useful for many applications, especially in Taguchi-type gas sensors as an active sensor material and in Lithium-ion batteries. For example, a nano-structured tin-based electrode can deliver a very high capacity (~700 mAhg⁻¹ at a rate of 8C) and still retain the ability to be discharged and recharged for 800 cycles [1].

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A tin-based amorphous oxide composite received in Fujifilm Celltec Co. provided more capacity than 600 mAhg⁻¹ with good cycling stability [2, 3]. After this report, tincomposites oxide drew much attention for the replacement of carbon or graphite as the anode in a battery cell. The advantages of the tin based oxide materials are greater specific capacity and higher density compared to graphite so that cells of higher specific energy can be built because tin can reversibly accommodate a maximum of 4.4 lithium atoms per tin atom, in the $Li_{22}Sn_5$ phase. This gives a theoretical specific charge capacity of 994 mAhg⁻¹, which is much higher than the 372 mAhg⁻¹ of fully-lithiated graphite (LiC₆).

Due to the substantially higher density of tin oxide the volumetric capacity is even more favorable than for graphite. The advantage of SnO_2 has been also proven in better cycle stability than the respective metal hosts [4]. In a tin-based oxide, the loss of capacity upon cycling occurred due to the degradation associated with the aggregation of tin atoms into clusters. As the clusters grow in size, they cause the material to fail for the same reasons as for bulk Li-Sn alloys. Results for crystalline SnO_2 indicate that smaller particles better cycling stability [5-7]. It was thought that tin is less prone to form large clusters if the crystal particles are very small. The initial lithium insertion involves an irreversible reduction of tin oxide into metallic tin, while the oxidation cycles during discharging involves a reversible reaction, which are represented by the following formulae:

$$4\mathrm{Li}^{+} + \mathrm{SnO}_2 + 4\mathrm{e}^{-} \rightarrow \mathrm{Sn} + 2\mathrm{Li}_2\mathrm{O} \tag{1}$$

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 $[\]Gamma dX$, + 62 - 2 - 2220 - 4011

$$xLi^{+} + Sn + xe^{-} \leftrightarrow Li_{x}Sn \ (0 \le x \le 4.4)$$
(2)

The AFD (Aerosol Flame Deposition) process is unique since it offers a route to prepare nano-porous samples composed of nano-sized particles [8]. Compared with other deposition technologies such as chemical vapor deposition (CVD) [9, 10], a sol-gel process [11], and other spray pyrolysis techniques [12,13], the advantages of this technique are a wide choice of nonvolatile precursors including liquid precursors and a high degree of crystallinity of the asprepared metal oxide nanoparticles [14, 15] due to the high reaction temperatures (2000-3000 K), and the capability to produce virtually all type of oxide nano powders that have been synthesized by solid state reactions. AFD also enables rapid formation of submicrometer and nano-sized metal oxide particles and the resulted deposition rate is very fast compared to the conventional synthesis techniques such as sputtering, a sol-gel process, CVD etc.

In this study we have synthesized tin-based composite amorphous oxides (SnO₂-P₂O₅-B₂O₃) by an AFD method and the obtained tin-based composite amorphous oxides obtained were tested for their anodic characteristics to verify the possibility for application in a lithium-ion battery.

Experiments

The AFD method was applied to fabricate anode powder of a tin-based amorphous oxide using the system shown in Fig. 1. In the AFD process, a liquid precursor solution was prepared by dissolving the desired precursors into a solvent and then atomizing them into micro-sized droplets by an ultrasonic nebulizer. The atomized droplets were carried by Ar carrier gas into a flame hydrolysis reaction zone in an oxy-hydrogen torch. The essential part of the system is the oxy-hydrogen torch, which is made from four concentric silica tubes creating three concentric gaps, and one shield tube keeping the flame stable. The precursor solution flows through the centermost tube of the torch while hydrogen, argon and oxygen flow through three gaps with a different width to ensure laminar flow of the gases supplied. The vapors of POCl₃ and BCl₃ produced by Ar bubbling under a controlled temperature were delivered to an oxy-hydrogen torch and hydrolyzed to form a porous oxide soot on Pt substrates. The synthesized soot powders were deposited at an oxygen flow rate of 7.5 L minute⁻¹, Ar shield flow rate of 2.5 L minute⁻¹ and hydrogen flow rate of 1.5 L/min. The flow rates of source gases were 20, 30, and 40 sccm. The notations for the specimens prepared are the abbreviation of the flow rate of these source gases for glass formers. For example, B10P20 denotes the specimen prepared at the flow rate of 10 sccm of BCl₃ and 20 sccm of POCl₃. To make a uniform deposit, tin-based oxide soot was first deposited on a substrate placed on a rotating stage, which was kept at 150 °C to eliminate the H₂O produced during hydrolysis. The whole processes were carried out under a normal air atmosphere with only optional control for the moisture. Then, the deposited soot was sintered at 550 °C for 6 h in an electric furnace. The structural and morphological changes were characterized using a X-ray diffractormeter (XRD) by Rigaku D/max-2500, with CuK_{α} X-ray radiation 40 mA 100 mV with a scanning step of 0.014 degree and an angle range from 20 to 80 degrees. As-deposited images of the sintered soot were taken using a scanning electron microscope (JEOL, JSM-6330F). The correlation between the structural modification of the glass network and the tin composition produced by heat treatment was characterized by Fourier Transform Infrared spectroscopy as a function of the chemical com-



Fig. 1. A schematic diagram of Aerosol Flame Deposition system for the synthesis of tin borophosphate oxide.

Galvanostatic charge/discharge cycling was conducted with coin cells prepared in an Ar-filled glove box. The negative electrode consisted of a tin-based oxide powder, acetylene black and IPA(isopropylalchole) on a copper foil. The resulting paste was pressed and then dried at 120 °C in a vacuum oven. Metallic lithium was used as a positive electrode. A non-aqueous solution of 1MLiPF6 in a 1 : 1 mixture of ethylene carbonate (EC)/diethyl carbonate(DEC) was used as the electrolyte(Samsung cheil industries). The coin cells were galvanostatically cycled in the voltage range of 0.02-1.5 V at room temperature.

Results and Discussion

Fig. 2 is a SEM image of tin oxide particles synthesized by the AFD method. It shows that the tin oxide powders prepared have a particle size of 20-50 nm. Fig. 3. is the surface of tin borophosphate oxide, which demonstrates that B_2O_3 and P_2O_5 particles were well mixed with SnO₂ particles.

Unlike conventional spray pyrolysis, the mechanism of particle formation is mainly the hydrolysis reaction



Fig. 2. SEM image of the synthesized SnO₂ powder.



Fig. 3. SEM image of tin borophosphate oxide(BCl₃ 10 sccm, POCl₃ 20 sccm) after calcination at 550 °C for 6 h.

for the formation of B_2O_3 and P_2O_5 [16]. For SnO₂, the mechanism is similar to that of spray pyrolysis. The synthesized particles are believed to be formed by the sublimation of precursors and the subseqent formation of a plasma due to the high temperature of the flame. Then, the gas phases produced by the high temperature flame experience gas phase nucleation, growth, and Brownian coagulation. The nucleation rate is dependent on the supersaturation of plasma gas phases and this supersaturation generally increases with the temperature gradient of the flame. Brownian coagulation would occur during the random flow of solid particles within the flame and causes the agglomeration of small particles, which increases the average particle size.

The rate of particle formation rapidly increases at the end of flame due to a reduced temperature. It was observed that small particles tend to agglomerate to a higher degree as shown in Fig. 2. The material system synthesized in this study did not exhibit the formation of relatively large particles (300-600 nm in diameter) which is a characteristic of direct pyrolysis of liquid precursor droplets. This observation suggests that the main synthesis mechanism of the material system studied is the gas phase nucleation and growth via the formation of a plasma.

 B_2O_3 and P_2O_5 are well known as glass network forming compounds and these are ion conductors acting as electrolytes. The anode material synthesized, therefore, is expected to be a mixture of SnO₂, an electronic conductor, and glass network forming compounds, as an ionic conductor.

In the reaction, the oxides particles formed were mainly amorphous oxides whose composition was determined by the proportion of the flow rates of BCl₃ and POCl₃. Fig. 4 gives XRD patterns of the synthesized powders deposited on Pt substrates at various flow rates of BCl₃ and POCl₃. It shows that the major peaks of the synthesized soot are well fitted to that of crystalline SnO₂(JCPDS 88-



Fig. 4. X-ray diffraction patterns of the SnO_2 - B_2O_3 - P_2O_5 powders synthesized at various flow rates of BCl₃ and POCl₃.

0287). The amorphous background increased with an increasing flow rate of BCl₃ and POCl₃, which is attributed to the formation of an amorphous phase of B_2O_3 and P_2O_5 . At the flow rate of B20P30, the crystalline peak of SnO₂ almost disappeared and this result suggests that the SnO₂ phase tends to be incorporated into the glass network of B_2O_3 and P_2O_5 . With an increase in the flow rate of BCl₃ and POCl₃, the crystalline H₃BO₃(JCPDS 30-0199) phase appeared due to the reaction with moisture within the oxyhydrogen flame or the atmosphere. Although the formation of H₃BO₃ is almost inevitable due to the hygroscopic nature of B_2O_3 , this phase was eventually converted into a B_2O_3 glass former during the heat treatment as will be discussed in the following.

Fig. 5. shows the X-ray diffraction patterns of the synthesized powders after calcination at 550 °C for 6 h. The comparison of these patterns to the corresponding patterns in Fig. 4 reveals that the crystalline peaks from SnO₂ diminished appreciably, which means that the amorphization of SnO₂ and the incorporation into the glass network has been undergone by the reaction with surrounding B_2O_3 and P_2O_5 powders. Therefore, except the B20P30 composition, the resulting microstructure of the sintered powder is a mixture of crystalline SnO₂ with amorphous B₂O₃-P₂O₅. One can also see that a minor peak of crystalline BPO₄($2\theta = 24^{\circ}$) was observable in the case of B20P30 composition [17]. Fig. 6 and the FTIR spectra of the as-deposited soot powder synthesized at various flow rates of BCl₃ and POCl₃. Hydrogen borate is shown in the IR spectra and XRD peak($2\theta = 14.5^{\circ}, 27.6^{\circ}$). The intensity of band at 1320-1580 cm⁻¹, assigned to the overlapped peak of the borate unit and the phosphates group, grew by increasing the flow rate of BCl₃ and POCl₃. The crystalline H₃BO₃ has sharp absorptions around 1200, 880, $650 \text{ and } 550 \text{ cm}^{-1}$ and the peak at 547, 2260, 2364 cm⁻¹



Fig. 5. The XRD patterns of the synthesized soot powders after calcination at 550 $^{\circ}$ C for 6 hrs. The soot powders were deposited on Pt substrates at various flow rates of BCl₃ and POCl₃.



Fig. 6. FTIR spectra of the soot powders synthesized at various flow rates of BCl₃ and POCl₃.

is also due to the B-O bond in H_3BO_3 [18]. The broad band at 1100 cm⁻¹ is attributed to the overlapped band of B-O and Sn-P-O. The band at 1450 cm⁻¹ is attributed to the overlapped band of B-O and P-O [19-21]. As expected, the band at 1100 cm⁻¹ increased with an increase in the flow rate of BCl₃ and POCl₃ due to the increased amount of B-O and P-O bonds. The peak at 648 cm⁻¹ is the Sn-O bond of SnO₂ and this band became smaller with the increasing flow rate of BCl₃ and POCl₃.

Fig. 7 and the IR spectra of the soot after calcination at 550 °C for 6 h. These spectra show that the O-H bond at 3200 cm⁻¹ was reduced significantly by calcinations. The 660 cm⁻¹ band is from the Sn-O bond of SnO₂ and this band became smaller with an increase in the flow rate of BCl₃ and POCl₃. The band at 1150 cm⁻¹ is thought to be the shifted overlapping band of B-O and Sn-O-P. This band grew significantly. The band at 1450 cm⁻¹ reduced



Fig. 7. FTIR spectra of the soot powders synthesized at various flow rates of BCl₃ and POCl₃ after calcination at 550 $^{\circ}$ C for 6 h.

significantly after calcination. These results suggest that the after calcination an appreciable amount of B_2O_3 , P_2O_5 , and SnO_2 phase had reacted each other and formed a homogeneous amorphous SnB20P30 specimen showing a B-P-O bond at ~950 cm⁻¹ due to BPO₄ [22].

From the comparison between Fig. 6 and 7, one can see that SnO_2 tends to absorb molecular water while B_2O_3 - P_2O_5 , tends to absorb water chemically in the form of OH. Fig. 8 give charge-discharge curves of the SnB10P20 specimen. The cycle tests were performed for 50 cycles between 0.02 V and 1.5 V at 0.3 mA. At first the charge capacity is very high about 2100 mAh/g. But after the second cycle, the charge capacity was measured to be 730 mAh/g. After 35 cycles, one can see in Fig. 9 that the discharge capacity was reduced to 240 mAh/g. The improved cyclability might be attributed to the nano-scale particle size, which would reduce the loss of Li ions due to the irreversible reaction of Li ions with SnO₂.

Conclusions

The SnO₂-B₂O₃-P₂O₅ composite oxide powders for anodes in Li-ion batteries were deposited by an aerosol flame deposition method at various compositions. The deposited



Fig. 8. Charge and discharge curves of the SnB10P20 composite oxide powder.



Fig. 9. Cycle performance of the SnB10P20 composite oxide.

powder contained amorphous B_2O_3 - P_2O_5 and crystalline SnO_2 . The microstructure of this composite was an interconnected porous mixture which is desirable for an anode application. The tin-based oxide electrode produced at a flow rate of 10 sccm of BCl₃ and 20 sccm of POCl₃ exhibited an improved cyclability and capacity. The retained capacity after 30 cycles was about 370 mAh/g. In this study, the aerosol flame deposition method demonstrated successfully the fabrication of the composite oxide anode powder and proved that this technique would open a new possibility for tin-based oxide as an anode material in Li-ion batteries.

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