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Mechanochemical synthesis of SnO-B_2O_3 glassy anode materials for rechargeable lithium batteries

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The xSnO·$(100 - x)B_2O_3$ $(0 \leqq x \leqq 80)$ glasses were successfully prepared by a mechanical milling technique. The glass with 40 mol% SnO showed the maximum glass transition temperature of 347°C. The SnO-B_2O_3 milled glasses consisted of both BO_3 and BO_4 units, and the fraction of BO_4 units was maximized at the composition of 50 mol% SnO. The electrochemical properties of the milled glasses were examined using a simple three electrodes cell with a conventional liquid electrolyte. The glasses with high SnO content exhibited high charge capacities more than 1100 mAh g^{-1} and discharge capacities more than 700 mAh g^{-1} at the first cycle. The SnO-B_2O_3 milled glasses proved to work as anode materials for rechargeable lithium batteries. *© 2004 Kluwer Academic Publishers*

1. Introduction

Lithium ion secondary batteries have been rapidly popularized as a power source for portable electronic devices such as video cameras, laptop computers and cell phones because the batteries have high energy density and lightweight. Novel electrode materials with higher capacity are desired in order to improve battery properties. SnO-based oxide glasses prepared by a conventional melt-quenching technique have been studied intensively as anode materials for rechargeable lithium batteries [1–5] because these glasses exhibit high specific capacities twice that of carbonaceous materials, which are commercially used as anode materials for lithium ion secondary batteries.

These SnO-based glasses were obtained by a mechanical milling technique using a high-energy ball-mill apparatus. We have succeeded in preparation of the $SnB_{0.5}P_{0.5}O_3$ glassy powder by mechanical milling, and confirmed that the glass worked as an anode material for rechargeable lithium batteries [6]. The mechanochemical synthesis has a favorable feature that fine powders are directly obtained without an additional pulverizing process of bulk glasses at room temperature.

In the present study, glassy anode materials in the simple binary system SnO-B_2O_3 were prepared by mechanical milling. Glass transition temperature and local structure of the milled glasses with wide compositions were investigated. The electrochemical properties of the milled glasses were examined using a simple three electrodes cell with a conventional liquid electrolyte.

2. Experimental

Reagent-grade chemicals of crystalline SnO (Furuuchi Chem., 99.9%) and amorphous B_2O_3 (Koujundo Chem., 99.9%) powders were used as starting materials for sample preparation. The mechanical milling treatment was carried out for the batches (2 g) of the mixed materials of xSnO·$(100-x)B_2O_3(0 \leqq x \leqq 85)$ in a zirconia pot (volume of 45 ml) with eight zirconia balls (10 mm in diameter) using a high-energy planetary ball mill apparatus (Fritsch Pulverisette 7). The rotation speed was fixed at 370 rpm and all the processes were conducted at room temperature in a dry N_2-filled glove box.

X-ray diffraction measurements (Cu K_α) were performed using a XRD diffractometer (Shimadzu, XRD-6000). Differential scanning calorimetry (DSC) was carried out using a DSC apparatus (Perkin Elmer, DSC7) for the obtained powder samples sealed in an Al pan in a dry N_2 atmosphere. The heating rate was 10 K/min in the temperature range from 25 to 500°C under N_2 atmosphere in all the measurements. Solid-state ^{11}B MAS-NMR spectra were recorded at 96.23 MHz on a UNITY INOVA 300 NMR spectrometer (Varian, UK). Detailed experimental conditions are given in [7].

Electrode materials were prepared by mixing the glassy powder (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in an agate mortar in a dry Ar-filled glove box. Slurries of the mixture were painted on a Ni mesh as a current collector and then dried. Electrochemical measurements were performed in a simple three-electrode cell with the obtained electrode as a working electrode and lithium sheets as counter and reference electrodes. A mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1:1 volumetric ratio containing 1 mol dm^{-3} (1M) $LiPF_6$ was used as an electrolyte.

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3. Results and discussion

XRD measurements showed that the $x\mathrm{SnO}\cdot(100-x)\mathrm{B_2O_3}$ amorphous materials were obtained in the composition range $0 \leqq x \leqq 80$ by mechanical milling for 100 h at room temperature. The SnO crystal as a starting material slightly remained at the composition of 85 mol% SnO even after mechanical milling for over 100 h. Glass-forming limit (higher SnO content) for the system SnO-B_2O_3 by the melt-quenching method was 75 mol% SnO [5].The amorphous material with 80 mol% SnO, which could not be obtained by melt-quenching, was prepared by mechanical milling.

Glass transition phenomena were observed on DSC curves for the prepared amorphous materials, and thus the amorphous materials obtained by mechanical milling proved to be in a glassy state. Fig. 1 shows the composition dependence of glass transition temperature (T_g) for the SnO-B_2O_3 glasses prepared by mechanical milling for 75 h (except for the composition of 80 mol% SnO which was milled for 100 h). The inset shows the DSC curve of the $50\mathrm{SnO}\cdot50\mathrm{B_2O_3}$ (mol%) milled glass as an example. The values of T_g increase up to 40 mol% SnO and then decrease with an increase in the SnO content. At the composition with 80 mol% SnO, T_g increases again. The glass with 40 mol% SnO shows the maximum T_g of 347°C.

The composition dependence of T_g for the milled glasses is almost the same as that for the corresponding melt-quenched glasses except for the compositions with higher SnO content; in the quenched SnO-B_2O_3 glasses, T_g increased up to 40 mol% SnO and then decreased with an increase in the SnO content [5]. However, the T_g values of the milled glasses are lower than those of the quenched glasses. For example, the $40\mathrm{SnO}\cdot60\mathrm{B_2O_3}$ (mol%) milled glass shows a T_g of 347°C while the corresponding melt-quenched glass exhibited a T_g of 384°C. Tsukushi *et al.* have also reported similar results that T_g of the glassy tri-O-methyl-β-cyclodextrin prepared by milling is lower than that of the corresponding melt-quenched glass [8]. They also mentioned that T_g of the milled glass tended to approach T_g of the melt-quenched glass with an increase in milling time. Although the difference on T_g between the quenched glasses and the milled glasses has not been understood well, the difference could be based on the inhomogeneity of the milled glasses, which is caused by the fact that the milled glasses are obtained from a solid-state interdiffusion process between particles [9] and not from an equilibrium melt state.

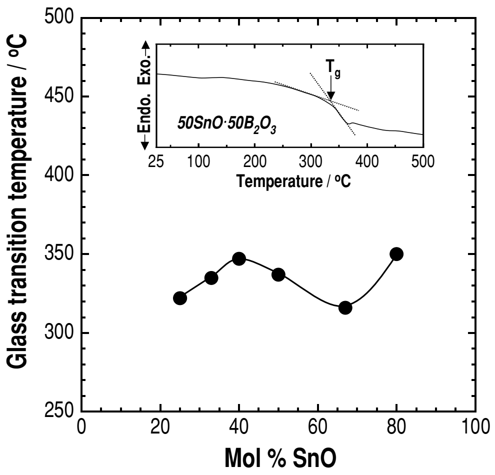

Figure 1 Composition dependence of glass transition temperatures (T_g) for the SnO-B_2O_3 glasses prepared by mechanical milling. The inset shows the DSC curve of the $50\mathrm{SnO}\cdot50\mathrm{B_2O_3}$ (mol%) milled glass.

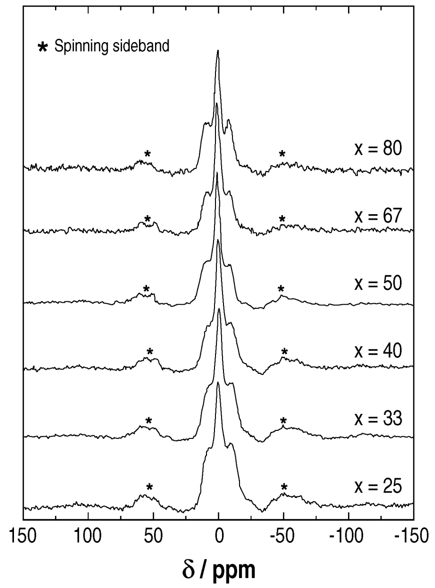

Figure 2 ^{11}B MAS-NMR spectra of the $x\mathrm{SnO}\cdot(100-x)\mathrm{B_2O_3}$ glasses prepared by mechanical milling.

Fig. 2 shows the ^{11}B MAS-NMR spectra of the $x\mathrm{SnO}\cdot(100-x)\mathrm{B_2O_3}$ glasses prepared by mechanical milling. Spinning sidebands are observed in the spectra and marked with asterisks in this figure. The sharp peak at 0 ppm is due to four-coordinated boron (BO_4 units) and the broad peak from −20 to +20 ppm is due to three-coordinated boron (BO_3 units) [10]. This figure indicates that both BO_4 and BO_3 units are present in the $x\mathrm{SnO}\cdot(100-x)\mathrm{B_2O_3}$ glasses prepared by mechanical milling. The fraction of BO_4 units (N_4) in the glasses was estimated by the relative area method proposed by Bray *et al.* [10]; we determined N_4 as the ratio of the area under the sharp peak to the area under the entire curve.

Fig. 3 shows the composition dependence of the N_4 values for the SnO-B_2O_3 glasses. Estimated

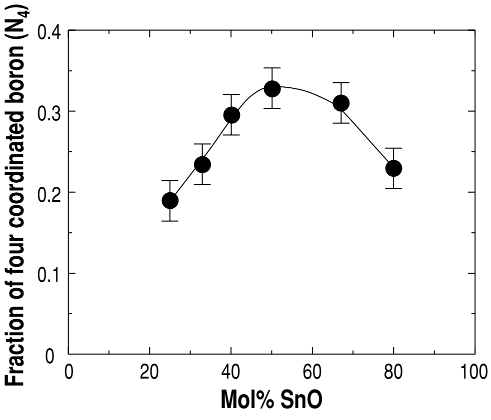

Figure 3 Composition dependence of fraction of four-coordinated boron (N_4) estimated from the ^{11}B MAS-NMR spectra of the $x\mathrm{SnO}\cdot(100-x)\mathrm{B_2O_3}$ glasses.

uncertainties are indicated by the error bars in this figure. The N_4 value increases and then decreases with an increase in the content of SnO. The maximum N_4 value of 0.33 ± 0.05 is obtained at the composition with 50 mol% SnO. The composition dependence of N_4 for the SnO-B_2O_3 glasses prepared by mechanical milling is quite similar to that for the glasses prepared by melt-quenching [7]. The N_4 value of the quenched glasses was also maximized at the composition with 50 mol% SnO, and the maximum N_4 value of 0.28 ± 0.05 is comparable to that of the milled glass under consideration of uncertainties. The local structure around boron atoms of the SnO-B_2O_3 milled glasses proves to be similar to that of the quenched glasses.

Charge-discharge measurements were performed using simple three-electrode cells with the SnO-based glasses as a working electrode. A constant current density of 1.0 mA cm^{-2} and a cutoff voltage between 0 and 2.0 V were used. Fig. 4 shows the first charge-discharge curves for the cells using the xSnO·$(100 - x)B_2O_3$ glasses prepared by mechanical milling. A charge corresponds to an insertion of lithium ions to the working electrode, while a discharge corresponds to an extraction of lithium ions from the working electrode. The abscissa shows the charge-discharge capacities per unit weight of the glasses. Two plateaus at around 1.5 and 0.5 V are observed on the charge curves and one plateau at around 0.5 V is observed on the discharge curves in the cells (except for the cell using the glass with $x = 25$). In the charge curve, the first plateau is due to the formation of metallic Sn^0 ($Sn^{2+} \rightarrow Sn^0$) and the second plateau is due to the formation of Li-Sn alloy ($Sn^0 \rightarrow$ Li-Sn) [1–4, 11]. The former reaction is known to be irreversible in SnO-based anode materials while the latter reaction is basically reversible. The SnO-B_2O_3 milled glasses prove to work as anode materials for rechargeable lithium batteries. The glasses with $x = 50$, 67 and 80 exhibit high charge capacities $>$1100 mAh g^{-1} and discharge capacities $>$700 mAh g^{-1}. In particular, discharge capacity and charge-discharge efficiency in the milled glasses of $x = 67$ and 80 are higher than those in the melt-quenched glasses [5].

Cycling behaviors of the cells using the xSnO·$(100 - x)B_2O_3$ glasses were also examined. Fig. 5 shows the cycle performance for the cell with the $50SnO{\cdot}50B_2O_3$ glass prepared by mechanical milling. Circles and triangles denote the charge-discharge capacities and charge-discharge efficiency, respectively. The cell exhibits the charge capacity of 1230 mAh g^{-1} and discharge capacity of 710 mAh g^{-1} at the 1st cycle. Both charge and discharge capacities gradually decrease with cycling while the charge-discharge efficiency increases. After 20 cycles the efficiency reaches 100% and the cell retains discharge capacity of 184 mAh g^{-1}. The $50SnO{\cdot}50B_2O_3$ melt-quenched glass showed almost the same discharge capacity of 200 mAh g^{-1} after 20 cycles [5]. In the cell with $80SnO{\cdot}20B_2O_3$ milled glass showed high discharge capacity of 757 mAh g^{-1} at the 1st cycle and, however, the capacity after 20 cycles was 135 mAh g^{-1}, which is lower than that of $50SnO{\cdot}50B_2O_3$. The B_2O_3 glass-matrix plays an important role in improving cyclability of SnO-based anode materials. The capacity fading with cycling on the milled glasses would be overcome by selecting appropriate voltage ranges. We confirmed that cycling performance of the cell using the $50SnO{\cdot}50B_2O_3$ melt-quenched glass was considerably improved by reducing the upper cutoff voltage from 2.0 to 0.8 V [5]. The formation of metallic Sn and its aggregation would occur in the voltage range over 0.8 V at the first discharge process [2]. The large volume change due to the aggregated Sn particles during charge-discharge cycling probably causes the degradation of capacity.

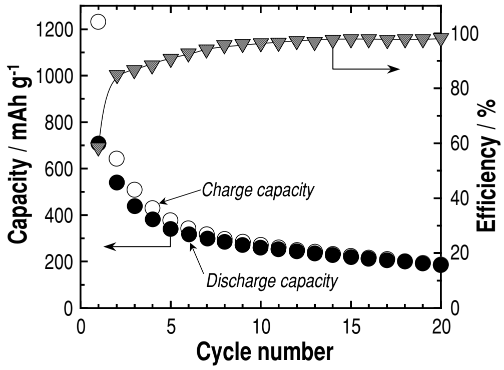

Figure 5 Cycle performances for the cells using the $50SnO{\cdot}50B_2O_3$ (mol%) glass prepared by mechanical milling. A constant current density of 1.0 mA cm^{-2} and a cutoff voltage between 0 and 2.0 V were used.

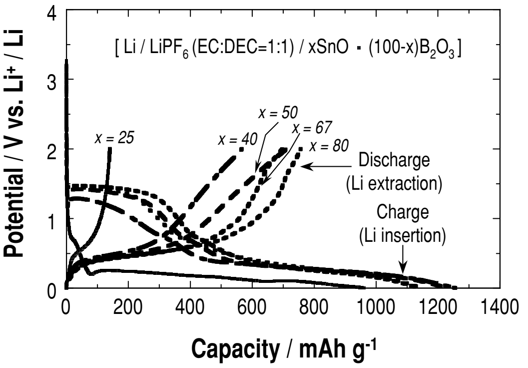

Figure 4 First charge-discharge curves for the cells using the xSnO·$(100 - x)B_2O_3$ glasses prepared by mechanical milling. A constant current density of 1.0 mA cm^{-2} and a cutoff voltage between 0 and 2.0 V were used. A mixture of 1 M $LiPF_6$/EC+DEC was used as an electrolyte.

4. Conclusions

The xSnO·$(100 - x)B_2O_3$ ($0 \leqq x \leqq 80$) glasses were prepared by mechanical milling. The glass with 40 mol% SnO showed the maximum T_g of 347°C and the composition dependence of T_g for the milled glasses was similar to that for the corresponding melt-quenched glasses. The SnO-B_2O_3 milled glasses consisted of both BO_3 and BO_4 units, and local structure around boron atoms in the milled glasses was almost the same as the corresponding quenched glasses. The electrochemical cells using the milled glasses were charged and discharged for 20 cycles under a constant current density of 1.0 mA cm^{-2} and a cutoff voltage between 0 and 2.0 V. The glasses with high SnO content exhibited high charge capacities $>$1100 mAh g^{-1} and discharge capacities >700 mAh g^{-1} at the first cycle. The cell with $50SnO \cdot 50B_2O_3$ glass retained discharge capacity of 184 mAh g^{-1} with the charge-discharge efficiency of 100% after 20 cycles. The SnO-B_2O_3 milled glasses as well as the quenched glasses proved to work as anode materials for lithium secondary batteries.

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