Formation of bismuth metal in bismuth borate glass by reductive heat treatment and its electrochemical property as anode in lithium ion battery

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The crystallization behavior of bismuth borate glass in hydrogen argon mixed atmosphere was examined. When the 70B2O3–30Bi2O3 glass prepared by the melt quenching method was heat treated in a 5% hydrogen-95% argon atmosphere, spherical bismuth metal particles were formed in the glass matrix at 380°C, which is higher than glass transition temperature at 336°C and close to crystallization temperature at 399°C. As increase of heat treatment temperature, the diameter of bismuth grain was increased. Electrochemical activity of bismuth metal containing glass-ceramics was also evaluated as a negative electrode in lithium ion battery. Suppression of irreversible capacity at initial cycle due to lithium insertion was successfully performed by reductive heat treatment for crystallization of bismuth metal into glass matrix.

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1. Introduction

Energy development plays an important role in the rapid growth of the global economy and is also indispensable in the progress of modern society. In recent years, new energy sources that do not depend on fossil fuels, such as solar or wind power, are attracting attention. However, since the output depends on the natural situation, appropriate energy storage/conversion technology is strongly required.1,2)

Lithium ion battery has both high energy density and power density, and provides a variety of characteristics such as high cycle performance and environmental compatibility, hence it has attracted attention as a power storage system.3,4) For efficiently larger power storage achievement, development of substitute electrodes is a promptly way. Even though commercial graphite-based anode has good capacities, the occurrence of dendrite formation on the anode surface during high rate cycling causes safety issues.

As substitute materials, alloy anode electrodes have extensively investigated and have large capacities. Alloy derived anode is essential not only for lithium ion batteries but also for development of sodium ion batteries.5–6) However, cycle performance must be improved because the metals undergo a significant volume change during lithiation due to the lithium insertion into the metal crystalline structure.7–9) Tin-phosphate glass (GSPO) anode solved some tin alloy anode’s problems with vitrification, which shows high energy density and great cycle performance in the wide operating temperature of −20–60°C.10) Kondo et al. proposed a crystallized GSPO with Sn particles prepared by reductively heat-treatment of GSPO with AlN as a reducing agent, and it improved its large irreversible problem.11) Besides, Honma et al.10) reported that GSPO works effectively as anode active materials for rechargeable sodium ion batteries.

Meanwhile, bismuth has a quite high volumetric capacity of 3765 mAh/cm³, instead of the relatively low gravimetric capacity of bismuth (386 mAh/g), which is comparable to that of the commercial carbon anode (372 mAh/g).12) Bismuth can make Li3Bi alloy formation with lithium at approximately 0.8 V (vs. Li/Li⁺), and established the good potentials with bismuth based compounds or composites.13–15) To our best knowledge, there is no literature on glassy Bi2O3 binary anode materials in lithium ion batteries. Bi2O3 easily get glassy state by mixing of another metal oxide, e.g. bismuth borate glass can contain much amount of Bi2O3 (~70 mol %) with ease and has been applied as a sealing glass due to its low melting point.16,17) It is also of interested to electrochemical properties because the Bi3⁺ ion can be coordination with 6–7 amount of O2⁻ ion on average in the glass and has
were used as separator. Test cells were assembled in an argon-filled glove box. The dew point of Ar atmosphere in the glove box was kept as $-86$°C and the oxygen content was less than 0.1 ppm. The solution of 1M-LiPF$_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v, Kishida Chemicals) was used as electrolyte. Cells were examined by using a battery testing system (Hokuto denko HJ1001SMA) at the charge/discharge current density of 1/10 C (38.4 mA/g) between 0 and 3.0 V.

3. Results and discussion

The appearances and DTA curves for bulk and powder-decorated 70Bi$_2$O$_3$–30B$_2$O$_3$ glass under an air atmosphere are shown in Fig. 1. It is seen that an endothermic dip due to the glass transition and several exothermic broad peaks are observed, providing the values of $T_g = 336$, $T_p = 437$ for bulk, and $T_p = 399$°C for powder, respectively. The difference of $T_p$ values between bulk and powder shapes means that the crystallization tends to occur from the glass surface. The appearances and XRD patterns for bulk and powder-decorated glass-ceramics obtained by heat-treatment at $437$°C for 3 h under an air atmosphere are shown in Fig. 2. Precipitated crystal phases were in agreement with a report of Levin et al. As the crystallization behavior, Bi$_2$O$_3$ crystal precipitated from glass surface and Bi$_4$O$_3$(BO$_3$)$_2$ crystal was confirmed as the main phase. The structure of Bi$_2$O$_3$ crystal was body-centered cubic with six-fold coordinated BiO$_6$ polyhedron, hence it categorized as $\gamma$-Bi$_2$O$_3$ crystal and it is of great interest because of its poor reports for the battery performances. Whereas, Bi$_4$O$_3$(BO$_3$)$_2$ crystal consists of asymmetric truncated BiO$_4$ and BiO$_5$ polyhedra and BO$_3$ triangles, and besides, generally known as Bi$_4$B$_2$O$_9$ crystal with the density of 8.17 g/cm$^3$. Note that Bi$_2$O$_3$ crystal consists of trivalent bismuth ions (Bi$^{3+}$) and its chemical composition corresponds to 66Bi$_2$O$_3$–33B$_2$O$_3$, being close to that of the precursor 70Bi$_2$O$_3$–30B$_2$O$_3$ glass. Bulk density of 70Bi$_2$O$_3$–30B$_2$O$_3$ glass was determined by Archimedes method at room temperature.
and was 7.777 g/cm³. Compared with Bi₂B₂O₉ crystal, it demonstrated lower density of 5% although containing surplus Bi₂O₃ in the glass system. It means that the glassy state can provide more advantageous ion diffusion property. On the other hand, the appearance of the specimen which is obtained at each heat treatment temperature of the 70Bi₂O₃–30B₂O₃ glass in a 5% hydrogen-95% argon atmosphere is shown in Fig. 3. The left side of the photograph shows the glass-ceramics powder from glass powder, and the right side of the picture shows the appearance after heat treatment of the bulk glass specimen. For the bulk sample, black darkening was observed in the sample subjected to reduction heat treatment at 380°C, suggesting the existence of reduced chemical species inside of glass. Deformation was observed in the sample annealed at 430°C or higher and metallic luster was confirmed on the bulk surface. For the powder samples, a black powder was obtained in the samples annealed at 380°C or higher. As the heat treatment temperature increased, fusion of the particles was confirmed and metal spheres were partially observed.

In order to investigate the change of morphology more closely, the scanning electron microscope images of samples as-prepared and heat treated glasses obtained by a milling is shown in Fig. 4. The shape of the particle was rounded and many spherical particles were observed for each powder sample heat-treated at 380°C or higher. On the other hand, the formation of spherical particles was also confirmed more clearly from the cleaved surface (cross-section of bulk) in heat-treated samples over 430°C as shown in Fig. 5. The number density as a function of particle diameter in the samples of heat-treated at 480 and 580°C is shown in Fig. 6. It clearly consisted of the spheres of sub-micrometer order in the sample heat-treated at 430°C. As increase of heat-treatment temperature, particle diameter varied from submicron to 5 μm. It was confirmed that coarsening occurs due to Ostwald ripening as the heat treatment temperature rises.

Figure 7 shows the XRD pattern of the powder sample obtained at each heat treatment temperature. Similarly to the XRD patterns as shown in Fig. 2, crystallization of Bi₂O₃ and Bi₄O₃(BO₃)₂ was confirmed in the sample annealed at 380°C. However, the diffractions from metallic bismuth was confirmed in the sample annealed at 430°C or higher. The element distribution on the surface of the sample annealed at 480°C is shown in Fig. 8. It is clear that the spherical particles are bismuth metal. Therefore, the reduction of bismuth in the 70Bi₂O₃–30B₂O₃ glass by annealing in hydrogen atmosphere starts above 380°C. It was revealed that the Bi³⁺ ions in the glass were reduced to the metallic state without softening and flowing of matrix phase. These results are quite different from tin phosphate glass, which is showing fluidity before tin metal particle due to their low glass transition temperature.

The charge and discharge curves for the lithium cathode of as quenched 70Bi₂O₃–30B₂O₃ glass and the sample formed with bismuth metal obtained by heat treatment at 580°C for 3 h are shown in Figs. 9 and 10. As shown in Fig. 9, several plateau voltages were confirmed in the initial charge curve approximately 1.9, 1.4, 0.6–0.8 V and in the initial discharge curve around 0.9 V, respectively. Regarding that of 1.9 V in the initial charge curve, it is considered that the reaction with Bi₂O₃ as shown in the formula (3.1) is due to the irreversible reaction of forming a matrix with lithium. This is supported by the report of Bi₂B₂O₉ crystal, Li₃BO₃ formation starts in 1.9 V and then Li₂O formation progresses at a lower potential. At around 1.4 V and a gently potential drop at 1.3–0.9 V, a reaction for reducing of Bi₂O₃ to Bi is progressing. Li et al. reported that the reaction formula (3.2, 3.3 in which the monoclinic α-Bi₂O₃ or tetragonal β-Bi₂O₃ is reduced to Bi proceeds 1.2 or 1.4 V.) However, from the crystallization behavior of this glass system, cubic Bi₂O₃ crystal was precipitated. Since there is no report on the lithium ion deintercalation behavior of cubic Bi₂O₃ crystal, this plateau may be unique to this glass. Regarding the potential at 0.8–0.6 V, it was attributed to both the progress of the alloying reaction of lithium and bismuth and the formation of the solid electrolyte interface (SEI) as shown.
Fig. 4. SEM images of powder samples obtained by reductive heat treatment.

Fig. 5. SEM images for the cross-sections of bulk specimen after cleaving and heat-treatment.
in the formula (3.4, 3.5). The former is reversible, whereas the latter is irreversible capacity loss.\(^{26}\)

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\begin{align*}
\text{B}_2\text{O}_3 + 6\text{Li} & \rightarrow 2\text{Li}_3\text{BO}_3, \quad E = 1.9 \text{ V} \quad (3.1) \\
\text{Bi}_2\text{O}_3\text{Bi}_{23} \text{(monoclinic)} + 4.66\text{Li} & \rightarrow 2\text{Bi} + 2.33\text{Li}_2\text{O}, \quad E = 1.4 \text{ V} \quad (3.2) \\
\text{Bi}_2\text{O}_3\text{Bi}_{23} \text{(tetragonal)} + 6\text{Li} & \rightarrow 2\text{Bi} + 3\text{Li}_2\text{O}, \quad E = 1.2 \text{ V} \quad (3.3) \\
\text{Bi} + \text{Li} & \rightarrow \text{LiBi}, \quad E = 0.75 \text{ V} \quad (3.4) \\
\text{LiBi} + 2\text{Li} & \rightarrow \text{Li}_3\text{Bi}, \quad E = 0.7 \text{ V} \quad (3.5)
\end{align*}
\]

Regarding the initial discharge curve, it is considered that the de-alloying process of \(\text{Li}_3\text{Bi}\) was progressing around 0.9 V. In addition, a gentle increase in potential was confirmed at 1.7–2.5 V, which was attributed to the oxidation reaction of Bi to \(\text{Bi}_2\text{O}_3\) as shown in Eq. (3.2).\(^{12,25}\) On the other hand, the initial charge capacity of the bismuth micro sphere dispersed glass-ceramics was 350 mAh/g.

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**Fig. 6.** Particle diameter distribution obtained from SEM images in heat-treated samples at 480 and 580°C as shown in Fig. 5.

**Fig. 7.** XRD patterns of 70Bi_2O_3–30B_2O_3 samples those are annealed under 5% hydrogen-95% argon.

**Fig. 8.** Elemental mapping images obtained by energy dispersive spectroscopy in glass-ceramics annealed at 480°C for 3 h.

**Fig. 9.** Charge and discharge profiles of 70Bi_2O_3–30B_2O_3 glass anodes.

**Fig. 10.** Charge and discharge profiles of bismuth dispersed crystallized glass annealed at 580°C for 3 h.
Since the capacities in the second cycle showed similar values of 230 mAh/g, the irreversible electrochemical reaction was successfully reduced by the formation of bismuth metal particles. To further improve the electrochemical properties, it is possible to add lithium oxides to the glass matrix, which is effectively reduce irreversible reaction expressed as Eqs. (3.1) and (3.2).

4. Conclusion

In conclusion, formation of bismuth metal by reduction heat treatment of 70Bi₂O₃–30B₂O₃ binary glass and electrochemical activity of the metal dispersed glass-ceramics as the anode active materials of the lithium ion batteries were also clarified. In the tin phosphate glass, there was a problem of softening at a much lower temperature than the optimum temperature zone for reduction to form tin metal. On the other hand, bismuth borate glass has a higher glass transition temperature than that of tin phosphate glass. Since the optimum temperature range to form metal particles in glass is very close to glass transition temperature in 70Bi₂O₃–30B₂O₃ glass, morphology control of bismuth metal particles in hydrogen atmosphere was easily achieved. Due to the reaction between the metal particles and the electrolyte solution, improvement of charge-discharge performance is required, but for the development of all solid state batteries the anode glass-ceramics will be the key material.

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