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Electrochemical performance as cathode of lithium iron silicate, borate and phosphate glasses with different Fe^{2+} fractions

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ABSTRACT

Lithium iron silicate glasses with different fractions of Fe^{2+} ions of $40Li_2O–10Fe_2O_3–50SiO_2$ (mol%) are prepared by conventional melt-quenching method and reducing heat treatment technique, and their electrochemical properties as cathode materials for Li^+ ion secondary batteries (LIBs: lithium ion batteries) are examined. It is demonstrated for the first time that $Li_2O–Fe_2O_3–SiO_2$ glasses work as cathode in LIBs, e.g., the discharge capacity at 100/C in the first cycle is 54.6 mAh g^{-1}. The heat treatment at 350 °C in 5% H_2/Ar induces not only the increase in the fraction of Fe^{2+} ions but also the increase in the packing density and the decrease in the electrical conductivity. It is clarified that the discharge capacity of the glasses is largely improved due to the increase in the fraction of Fe^{2+} ions. The data on thermal, physical, and discharge properties obtained in $40Li_2O–10Fe_2O_3–50SiO_2$ glasses are compared with those in borate and phosphate glasses of $40Li_2O–10Fe_2O_3–50(B_2O_3, P_2O_5)$.

1. Introduction

Lithium ion battery (LIB) is becoming one of the very important batteries in the present society, because LIB has the biggest energy density in rechargeable batteries [1]. Goodenough et al. [2] reported the function of LIB cathodes used $LiCoO_2$ crystal in 1980, and then $LiCoO_2$ has been used commercially as cathode materials for current LIBs. Although $LiCoO_2$ has some benefits such as high energy density, this crystal has also some disadvantages such as high materials cost and low thermal stability. In recent years, applications of LIBs have been considered from energy storage devices of mobile-type equipments such as laptop to large energy storage devices such as electric vehicle. The large energy devices need the development of new cathode materials with safety, low materials cost, and high energy density. Therefore, it is of very importance to explore alternative materials for $LiCoO_2$, and indeed, various new materials including crystals, amorphous, and organic compounds have been reported.

$LiFePO_4$ crystal reported by Padhi et al. [3] has received much attention as an alternative cathode material in LIBs for $LiCoO_2$. It is noted that $LiFePO_4$ crystal consists of Fe being an abundant element in the earth crust. Furthermore, $LiFePO_4$ crystal with a poly-anion structure has a good thermal stability during the charging state when compared with $LiCoO_2$ crystal [4]. Recently, a spinel-type new $LiFeSiO_4$ crystal was developed through the rapid quenching of a melt with the composition of $25Li_2O–25Fe_2O_3–50SiO_2$ (mol%) by Honma et al. [5]. It is noted that $LiFeSiO_4$ has a high electrical conductivity of $\sigma = 2.5 \times 10^{-4}$ S cm^{-1} at room temperature. Furthermore, the melt-quenching method is very simple and easy when compared with conventional solid state reaction method, because this method is a one-step preparation method (melting and quenching) and usually enables the preparation of materials by short time. These advantages would be important in practical (commercial) production of LIBs.

Sakurai et al. [6] reported the recharge-ability and good cycle-ability of $V_2O_5–P_2O_5$ glasses as cathodes for LIBs, which is the first report on the glass-based cathodes for LIBs. After this report, some researches on the recharge-ability of Mo–V–P–O glasses [7] and Li–Fe–P–B–O glasses [8] were carried out. In addition, Pistoia et al. [9] demonstrated that the glassy cathodes based on $Li_2O–V_2O_5$ glasses exhibit better actual capacity and cycle-ability when compared with $Li_{1+x}V_3O_8$ crystals. It should be pointed out that their studies on glass-based cathodes reported so far are mainly for the systems based on V_2O_5, P_2O_5, and B_2O_3, and there has been no report on glassy SiO_2-based cathodes. Because a molecular weight (M_w) of SiO_2, $M_w = 60.1$ g mol^{-1}, is smaller than those of other glass network formers, e.g., $M_w = 181.9$ g mol^{-1} of V_2O_5, $M_w = 141.9$ g mol^{-1} for P_2O_5, and $M_w = 69.6$ g mol^{-1} for B_2O_3, the so-called theoretical capacity (i.e., capacity per unit mass, mAh g^{-1}) in glassy SiO_2-based cathodes would be expected to be large when compared with other V_2O_5-based and P_2O_5-based glasses with similar glass composition. Furthermore, SiO_2-based materials are present abundantly as natural resources in the earth crust when compared with other glass formers. Therefore, it is of importance to study the recharge-ability of glassy SiO_2-based LIB cathodes and to clarify whether SiO_2-based glasses containing Li^+ ions work as LIB cathodes or not.

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In this paper, a glass with the composition of $40Li_2O–10Fe_2O_3–50SiO_2$ (mol%), i.e., as-prepared glass, was synthesized by using a conventional melt-quenching method. This composition is located at the edge of the glass-forming region in the ternary $Li_2O–Fe_2O_3–SiO_2$ system [10]. Furthermore, glasses with different fractions of Fe^{2+} ions were prepared by heat treatment of the as-prepared glass in a reducing atmosphere, i.e., heat-treated glasses. The electrochemical properties of the as-prepared and heat-treated glasses were measured to clarify their battery performance. We also examined the electrochemical properties of $40Li_2O–10Fe_2O_3–50P_2O_5$ and $40Li_2O–10Fe_2O_3–50B_2O_3$ glasses in order to compare the contribution of other poly-anions such as borate and phosphate to battery performance.

2. Experimental

The glasses of $40Li_2O–10Fe_2O_3–50(SiO_2, B_2O_3, P_2O_5)$ (mol%) were prepared by using a conventional melt-quenching method. Reagent grade commercial powders of Li_2CO_3 (Reagent grade, Nacalai Tesque), Fe_2O_3 (99%, Kojundo Chem.), SiO_2 (Reagent grade, Nacalai Tesque), B_2O_3 (>99.9%, Kojundo Chem.), and H_3PO_4 (Reagent grade, Nacalai Tesque) were used as raw materials. The raw materials were mixed and melted in a platinum crucible at 1100–1400 °C for 25 min in air. In case of phosphate, the mixtures were heated at 130 °C for 2 h to induce the dehydration of H_3PO_4 before melting. The melts were poured onto an iron plate and were pressed by another iron plate to a thickness of about 1 mm. The quenching rate of melts was around 10^6 K min^{-1} [10]. In order to prepare the glasses with different fractions of Fe^{2+} ions and to clarify the effect of the valence state of Fe ions on electrochemical properties, as-prepared glass plates with polished surface and composite powders of glasses and carbon were heat-treated at 350 °C or 400 °C for 10 h in 5% H_2/Ar.

Differential thermal analysis (DTA) (Rigaku TG-8120) and X-Ray diffraction (XRD, Rigaku Ultima IV) analysis were carried out for the as-prepared and heat-treated samples to clarify the glass formation and to determine the glass transition (T_g) and crystallization peak (T_p) temperatures. Densities of as-prepared and heat-treated glasses were measured by the Archimedes method with kerosene (Reagent grade, Nacalai Tesque) as an immersion liquid. The fraction of Fe^{2+} ions, $R(Fe^{2+}) = Fe^{2+}/(Fe^{2+} + Fe^{3+})$, in the as-prepared and heat-treated glasses was determined from X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI5000 Versa Prove II) which has monochromatic Al Ka X-rays (1486.6 eV) as an excitation source. The conditions used for all spectrum measurements were as follows: the pass energy was 58.7 eV and the X-ray spot size was a diameter of 100 μm with the energy of 25 W. Electrical conductivities of as-prepared and heat-treated glasses were measured by an alternating current (AC) impedance method (HIOKI 3522-50 LCR HiTESTER) in the temperature range from room temperature to 250 °C. Metal gold was sputtered to the glass surface as electrodes (ULVAC QUICK COATER VPS-020).

The charge/discharge tests for as-prepared and heat-treated glasses were carried out by following procedures. First, as-prepared glasses were pulverized by milling, and glass powders obtained were mixed with carbon by planetary ball milling (Premium line P-7, Fritsch Co.) at 800 rpm for 100 min. Second, poly-vinylidene-difluoride (PVDF #1100, Kishida Chemical Corp.) and proper amount of N-methyl-2-pyrrolidone (99.0%, Kanto Chemical Co.) were added to glass/carbon composite powders, and slurries obtained were spread on aluminum foils by a bar coater. The weight ratio of the mixtures in the cathode was 83.3 wt.% for the samples, 8.3 wt.% for carbon, and 8.3 wt.% for PVDF. The sheets were dried at 80 °C for 1 h, and circular disks as cathodes were prepared by cutting the sheets. Test cells were assembled using the disk as a cathode, a lithium metal as an anode, and a solution of 1 mol/L $LiPF_6$ in ethylene carbonate: diethyl carbonate, EC:DEC (1:1, by vol.%) (Kishida Chemical Corp.) as an electrolyte in Ar atmosphere (RH% < 2.0×10^{-3}). The electrochemical performance was tested from charge/discharge measurements (HJ-1001, Hokuto denko) at 25 °C. The cell potential was swept in the range of 1.5–4.3 V, and the charge/discharge rate was C/100 or C/10.

3. Results and discussion

3.1. Glass formation and characterization of glasses

The homogeneous melt-quenched samples with the compositions of $40Li_2O–10Fe_2O–50(SiO_2, B_2O_3, P_2O_5)$ were obtained by a conventional melt-quenching method. The volatile components such as Li_2O, B_2O_3, and P_2O_5 might partially vaporize during the melting. The chemical compositions of the as-prepared samples have not been analyzed in this study, and the nominal compositions are used in this paper. Fig. 1 shows XRD patterns for the as-prepared samples, indicating only haloes without any sharp diffraction peaks. Fig. 2 shows DTA profiles for the as-prepared samples in powder and bulk forms. The endothermic dips due to the glass transition and exothermic peaks due to the crystallization are clearly observed. The values of T_g and T_p determined for the bulk samples are summarized in Table 1. The results shown in Figs. 1 and 2 indicate that all the melt-quenched sample of $40Li_2O–10Fe_2O–50(SiO_2, B_2O_3, P_2O_5)$ are regarded as glass.

The XRD patterns for the glass powders and carbon composite samples obtained by heat treatments at 350, 400, and 450 °C for 3 h in 5% H_2/Ar atmosphere are shown in Fig. 3. The following information on the crystallization was obtained. In case of $40Li_2O–10Fe_2O_3–50SiO_2$ glass, the sample heat-treated at 350 °C keeps still the glassy state, but the sample heat-treated at 450 °C shows some XRD peaks, indicating the formation of crystals. At this moment, the crystalline phase formed was not identified, i.e., an unknown phase. However, it was found that the XRD pattern of this unknown phase is very resemble to that of Ta_2C crystal (ICDD: 01-073-1321). In case of $40Li_2O–10Fe_2O_3–50B_2O_3$ glass, the sample heat-treated at 450 °C shows the formation of Fe_3O_4 crystals (ICDD: 01-077-1545), and an unknown phase being different from that in $40Li_2O–10Fe_2O_3–50SiO_2$ glass is also formed. In case of $40Li_2O–10Fe_2O_3–50P_2O_5$ glass, $LiPO_3$ (ICDD: 01-074-4881) and $Fe_2P_2O_7$ (ICDD: 01-072-1516) crystals were formed in the sample heat-treated at 450 °C. The XRD patterns shown in Fig. 3 clearly indicate that the heat-treatments at 350 °C (SiO_2-based and B_2O_3-based glasses) and at 400 °C (P_2O_5 glass) for 3 h in 5% H_2/Ar atmosphere do not induce any crystallization, keeping the glassy state. In order to confirm this behavior, the as-prepared glasses were heat-treated for a more prolonged time of 10 h, and the XRD patterns for the samples obtained are shown in Fig. 4. Any sharp XRD peaks were not observed in these samples,

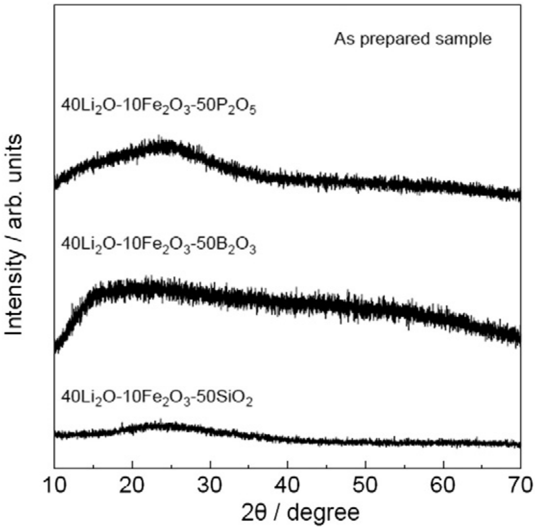

Fig. 1. XRD patterns at room temperature for the powders of as-prepared samples with $40Li_2O–10Fe_2O_3–50(SiO_2, B_2O_3, P_2O_5)$ (mol%).