Vanadium coordination environment in phospho-vanadate glass for improving water durability

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Understanding the mechanism behind the water durability improvement of phospho-vanadate glass is crucial for enabling the practical use of low-melting glass in lead-free sealing and secondary ion batteries. We demonstrate that Fe2O3 additive is a key component for improving the water durability while suppressing the rise of the glass transition temperature of V2O5–P2O5 (VP) glass, and characterize the local structural change by X-ray absorption fine structure measurements. In VP glass, the addition of Fe2O3 increases the coordination number of vanadium ion without changing the oxidation state. The water durability is relatively sensitive to the vanadium valence and coordination environment compared to the glass transition temperature and hardness. Minimizing V⁵⁺O₄ units in phospho-vanadate glass is the key to improving the water durability.

Key-words : Phospho-vanadate glass, Water durability, Oxidation state, XAFS, Local structure

1. Introduction

Oxide glassy materials are primarily divided into three categories: network formers, network modifiers, and intermediates.1,2) V2O5 is classified as a network former or intermediate, and it is hard to form glass on its own. Several components can vitrify V2O5 in binary systems.3) Semiconducting vanadate glass is quite attractive not only as an electrode material for secondary ion batteries4) but also as low-melting glass for lead-free sealing5) due to its low glass transition temperature and relatively low thermal expansion. However, there are two critical issues hampering its practical use: poor water durability and low thermal stability.

In our previous study,1,2) we characterized the atomic structure of V2O5–P2O5 (VP) binary glass by reverse Monte Carlo modelling based on neutron/synchrotron X-ray diffraction (XRD) and V K-edge extended X-ray absorption fine structure (EXAFS) data. We investigated the water durability of the binary glass and found that reducing the V⁵⁺O₄ units is crucial for improving water durability because these units seem to be highly reactive towards water. In the binary glasses, the water durability was improved by changing V⁵⁺O₄ units to V⁴⁺O₄ units, which is an unusually small coordination number in the tetravalent vanadium state, due to the increase of P2O5 amount. On the other hand, the increase of V⁴⁺O₄ units due to the amount of P2O5 increase seems to increase the glass transition temperature, which is not preferable for sealing.

Hence, in the present study, we selected Fe2O3 additives as a component of improving the water durability while suppressing the rise of the glass transition temperature, and investigated the relationship between the properties and local structural change of VP glass.

2. Experimental procedures

Sample preparation. Glass samples with a nominal molar composition of (100 − x) (81V2O5–19P2O5) –
xFe₂O₃ (VPFx) were synthesized by melt quenching of V₂O₅, P₂O₅, and Fe₂O₃ powders (Kojundo Chemical Laboratory Co., Ltd.). In order to clarify the effect of Fe₂O₃ additives, the V₂O₅/P₂O₅ ratio known to affect water durability was made constant. One hundred grams of the mixture was melted at 1000 °C in a platinum crucible and kept at that temperature for one hour. The molten glasses were cast onto a stainless-steel plate at 100 °C. The prepared samples were annealed at 10 °C higher than the glass transition temperature and slowly cooled at 1 °C min⁻¹ for 40 min to relieve internal stress.

**Characterization.** The resulting materials were fully amorphous, as confirmed by XRD using a diffractometer system equipped with a monochromatic CuKα radiation source (Rigaku, RINT-2000). The cation compositions of the resulting materials were determined with an accuracy of ±0.5 mol% by wavelength dispersive X-ray fluorescence spectrometers (Rigaku, ZSX Primus II). The fraction of the reduced amount of V ion ([V⁴⁺]/[V_{total}]) was estimated with an accuracy of ±0.01 by measuring the quantities of pentavalent vanadium ions [V⁵⁺] and total vanadium ions [V_{total}] by oxidation-reduction titration, assuming that the V ions in the glass consisted of V⁵⁺ and V⁴⁺. The densities of the glass samples were measured using a dry pycnometer (Micromeritics, AccuPyc II 1340) with an accuracy of ±0.0004 g cm⁻³. The atomic number densities of these samples were calculated from the density and the V⁴⁺/V_{total} ratio. The apparent molar volumes of O ions were also calculated from the density and the V⁴⁺/V_{total} ratio using the formula described by Drake et al.¹³) The glass transition temperature (T_g) was measured with an accuracy of ±2 °C using differential thermal analysis (DTA) (Advance Riko, DT-1500) at a heat rate of 5 °C min⁻¹. The weight loss in water at 70 °C for 30 min for the glass sample plates was measured to determine the water resistance, and the average of three measurements was plotted. Vickers microhardness measurements were performed on the sample surfaces at room temperature using an auto hardness test system (Matsuzawa, AMT-X7FS) with an accuracy of ±0.04 GPa. A load was applied for 0.98 N, 15 s.

**Structure analysis of glass.** X-ray absorption fine structure (XAFS) experiments were carried out using the BL14B2 (Fe K-edge spectra) and BL16B2 (V K-edge spectra) beamline of SPring-8.¹⁴) The XAFS samples for V K-edge spectra were ground with boron nitride and formed into pellets. V K-edge spectra were measured using a Si(111) double-crystal monochromator in transmission mode while Fe K-edge spectra were measured in fluorescence mode. The quick scan technique (QXAFS) was used for both of these measurements. These spectra were normalized and analyzed using Athena in the Demeter software package.¹⁵) The background was subtracted using the pre-edge linear range of -150 to -30 eV (relative to E₀) and the linear post-edge region at the V K-edge and the Fe K-edge of 150 to 850 eV, 150 to 1283 eV (relative to E₀), respectively. E₀ at V K-edge and Fe K-edge were set at 5465, 7117 eV, respectively. The over-absorption effect of the Fe K-edge spectra was corrected by Athena.¹⁵) The EXAFS oscillations of vanadium and iron ions, χ(κ), were extracted using Athena.¹⁵) All analyses were performed with the k³χ(κ) signals. To obtain the so-called pseudo-radial distribution function, the k³χ(κ) signals of vanadium and iron were Fourier transformed (FT) over the 3.0–12 Å⁻¹ and 2.0–9.0 Å⁻¹ k-ranges, respectively. The curve-fitting procedure with Artemis¹⁵) was used to determine the Debye–Waller factors (σ²), coordination numbers (CN), and bond lengths for the first coordination shell. The curve fitting of V K-edge and Fe K-edge spectra were carried out in real (r) space from 0.9 to 2.3 Å and 1 to 2 Å, respectively.

**3. Results**

Glass compositions of the VPFx glass samples are summarized in **Table 1.** DTA curves of the VPFx glass samples are shown in **Fig. 1(a).** The glass transition temperatures T_g determined from Fig. 1(a), which are also summarized in Table 1, suggest that T_g increased as the Fe₂O₃ amount increased. These glasses do not show clear crystallization temperature T_c, but T_c are at least above 300 °C. Although we cannot discuss the thermal stability ΔT = T_c – T_g, it seems not to be a significant difference. Figure 1(b) shows the normalized weight loss in water and Vickers microhardness of these glass samples. The water durability improved dramatically, while the glass hardened slightly as the Fe₂O₃ amount increased. These results suggest that the addition of Fe₂O₃ can greatly improve the water durability without significantly affecting the thermal properties or hardness of the VP glass.

The density and the fraction of V⁴⁺/V_{total} for these samples are shown in **Fig. 2(a).** The density increased as the Fe₂O₃ amount increased. Although the fraction of V⁴⁺/V_{total} was slightly decreased as the Fe₂O₃ amount increased, it was mostly independent of Fe₂O₃ amount. Figure 2(b) shows the atomic number density and apparent molar volume of O ion calculated from the density and the fraction of V⁴⁺/V_{total}. The atomic number density barely changed with the Fe₂O₃ amount, and therefore, the apparent molar volume of O ion increased as the Fe₂O₃ amount increased because the ratio of O is smaller than that of cations as compared to V₂O₅ or P₂O₅.

The XANES, EXAFS k³χ(κ), and FT EXAFS spectra at the V K-edge for a series of VPFx glasses are summarized in **Fig. 3.** Although the absorption energies (defined at half height) of the spectra [Fig. 3(a)], which indicate the vanadium oxidation state, were slightly shifted to the high

**Table 1.** Composition and glass transition temperature of VPFx glasses

| Sample no. | Composition (mol %) ± 0.5 | P₂O₅/(V₂O₅ + P₂O₅) (%) | Glass transition temperature (°C) ± 2 |
|------------|---------------------------|--------------------------|-------------------------------------|
| VPF0       | 81.8 18.2 18.2            | 18.2                     | 240                                 |
| VPF2       | 80.0 18.5 1.5             | 18.8                     | 244                                 |
| VPF7       | 75.8 17.1 7.1             | 18.4                     | 255                                 |
| VPF13      | 70.5 16.4 13.1            | 18.9                     | 279                                 |
energy side as the Fe$_2$O$_3$ amount increased, they barely changed with the Fe$_2$O$_3$ amount. This result is consistent with the results of the V$^{4+}$/V$_{\text{total}}$ ratio [Fig. 2(a)]. On the other hand, the FT EXAFS spectra [Fig. 3(c)] show significant composition-dependent modification of the V–O local environment. As the Fe$_2$O$_3$ amount increased, the peak top intensities of the FT EXAFS spectra increased and the peak top positions shifted slightly longer. This result indicates that the average CN of vanadium ions is increased with the amount of Fe$_2$O$_3$ content without changing the vanadium valence. Figure 3(d) shows the calculated amplitude reduction factor $S_0^2$ under a fixed Debye-Waller factor from the FT EXAFS spectra at the V K-edge [Fig. 3(c)]. Although the error bars of the analysis are large, we conclude that the CN increased with the amount of Fe$_2$O$_3$ content because the pseudo-radial distribution functions clearly changed. The amplitude reduction factor $S_0^2$ is the same for each sample, which indicates that CN is increased by 5.5% between VPF0 and VPF13. Taking our previous study into account, the VO$_x$ polyhedra are divided into six units, V$^{4+}$O$_{4.6}$ and V$^{5+}$O$_{4.6}$. Because the vanadium valence does not change and the amount of V$^{4+}$ ion is small, the main structural change is the change of V$^{5+}$O$_4$ units to V$^{5+}$O$_5$ or V$^{5+}$O$_6$ units. Figures 4(a)–4(c) summarizes the XANES, EXAFS $k^2\chi(k)$, and FT EXAFS spectra, respectively, at the Fe K-edge for a series of VPFx glasses. All three spectra are almost identical for each sample. Thus, the local environment of iron ion in the VPFx glasses does not depend on the Fe$_2$O$_3$ amount. The absorption energies of the sample’s spectra are located higher than that of the Fe$_2$O$_3$ spectrum. While the reason for this is not clear, at least the valence of iron was estimated to be trivalent. The CN of iron ion can be adjusted to six coordinates by fitting to FT EXAFS spectra. However, it is known that Fe$^{3+}$ also has four coordination in iron phosphate glass. Therefore, although the CN cannot be determined only from this result alone, there is no change in CN, at least depending on the Fe$_2$O$_3$ amount.

4. Discussion

We set out to analyze the local structure of vanadium and iron ions in order to clarify the effect of Fe$_2$O$_3$ addition. Our findings show that the addition of Fe$_2$O$_3$ increases the
coordination number of vanadium ions without changing the oxidation state and improves the water durability of VPFx glass. The EXAFS and oxidation-reduction titration analysis suggest that the main factor behind this improvement is the structural change of the $V^{5+}O_4$ units to $V^{5+}O_5$ or $V^{5+}O_6$ units. The results are consistent with our previous
study, where we found that the V$_{5+}$O$_4$ units are highly reactive towards water.\textsuperscript{12} Therefore, the mechanism for improving water durability in phospho-vanadate is to reduce the V$_{5+}$O$_4$ units, for example, by changing them into V$_{4+}$O$_4$, V$_{5+}$O$_5$, or V$_{5+}$O$_6$.

Figure 5 shows a comparison of the property changes with V$_2$O$_5$ amount between VP glasses\textsuperscript{12} and VPF$_x$ glasses. At around 70 mol% V$_2$O$_5$ content, the water durability of the VPF$_x$ glasses is superior to that of the VP glasses, while the glass transition temperatures are almost identical. This indicates that the addition of Fe$_2$O$_3$ can improve the water durability while suppressing the rise of the glass transition temperature. We also found that, within the scope of this study, the glass transition temperature and Vickers microhardness depend on the amount of V$_2$O$_5$ regardless of the difference of vanadium valence and coordination environment. Namely, these properties are relatively insensitive to the vanadium valence and coordination environment as compared to the water durability. Although the relationship between the glass transition temperature and the atomic structure of glass is still unclear, we do know that the hardness seems to be affected by atomic packing density and dissociation energy per unit volume component.\textsuperscript{17} Therefore, we conclude that the difference in vanadium valence and coordination environment in this study has little effect on atomic packing density and dissociation energy per unit volume component.

These results indicate that the water durability is especially sensitive to the vanadium valence and coordination environment, and they are quite sensitive to the additives. In other words, properly utilizing the additives can help overcome the problem of water durability for practical use of vanadate glass. On the other hand, considering our previous study,\textsuperscript{12} V$_2$O$_5$ acts as a network former in the composition range of this study, so these results might be limited to the composition in which V$_2$O$_5$ acts as a network former.

5. Summary

In this paper, we used XAFS measurements to clarify the mechanism behind improved water durability while suppressing the rise of glass transition temperature by Fe$_2$O$_3$ additives. Adding Fe$_2$O$_3$ affects the local structure of vanadium ions, which act as a network former, without changing the oxidation state. We conclude that the water durability is especially sensitive to vanadium valence and coordination environment and that minimization of the V$_{5+}$O$_4$ units by additives is important to improve the water durability. Our findings are significant in terms of advancing the practical use of vanadate glass: for example, to make glass sealing materials lead-free and to fabricate cathode materials for secondary batteries. Furthermore, the results may also help to provide a better understanding of semiconductivity.
Acknowledgments

The synchrotron radiation experiments were performed at BL14B2 and BL16B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal Nos.2018B2083, 2018B5400, 2019A5400). The authors thank Dr. H. Ofuchi for his assistance in the measurements and data analysis.

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