

Electrical conductivity and local structure of lithium iron tungsten vanadate glass

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Abstract A relationship between physical properties and local structure of $20\text{Li}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ glass, abbreviated as $x\text{LFWV}$ glass ($x = 0 - 25$ in mol%), was investigated by ^{57}Fe -Mössbauer spectroscopy, Fourier transform infrared spectroscopy (FT-IR), differential thermal analysis (DTA), leaching test using 20 vol% HCl and DC two- or four-probe method. ^{57}Fe -Mössbauer spectra of $x\text{LFWV}$ glass showed an increase of quadrupole splitting (Δ) from 0.67 to $0.73_{\pm 0.02}$ mm s^{-1} and a constant isomer shift (δ) of $0.39_{\pm 0.01}$ mm s^{-1} with an increase of 'x' from 0 to 25. This suggests that $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra gradually increase their local distortion along with a substitution of WO_3 for V_2O_5 . DTA of $x\text{LFWV}$ glass showed an increase in glass transition temperature (T_g) from 252 to $298_{\pm 5}^\circ\text{C}$ with an increase of 'x'. Composition dependency of T_g and Δ indicates that Fe^{III} atoms occupy substitutional sites of WO_6 octahedra as network former (NWF), since a large slope of $680\text{ K}(\text{mm s}^{-1})^{-1}$ was obtained in $T_g - \Delta$ plot. Comparable electrical conductivities (σ) of 2.5×10^{-6} , 1.9×10^{-6} , 8.4×10^{-7} and $2.9 \times 10^{-6}\text{ S cm}^{-1}$ obtained for $x\text{LFWV}$ glasses with 'x' of 0, 10, 20 and 25, respectively increased to 2.4×10^{-2} , 2.4×10^{-3} , 3.5×10^{-4} and $8.8 \times 10^{-5}\text{ S cm}^{-1}$ after annealing at 400°C for 100 min. Smaller Δ values of 0.58 and $0.67_{\pm 0.02}$ mm s^{-1} obtained in annealed $x\text{LFWV}$ glasses

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with 'x' of 0 and 10, respectively indicate that structural relaxation occurs in VO₄ units of vanadate glass units, as had been observed in other vanadate glasses.

Keywords Lithium iron tungsten vanadate glass · ⁵⁷Fe-Mössbauer spectroscopy · Electrical conductivity

1 Introduction

Vanadate glass is known as a semiconductor with an electrical conductivity (σ) of 10^{-7} – 10^{-5} S cm⁻¹ caused by 3d electron (polaron) hopping from V^{IV} or V^{III} to V^V [1]. It was reported that a drastic increase in the electrical conductivity (σ) took place in semiconducting barium iron vanadate glass, e.g., 20BaO·10Fe₂O₃·70V₂O₅ glass from 10^{-7} to 10^0 S cm⁻¹ when annealing temperatures higher than glass transition temperature (T_g) or crystallization temperature (T_c) [2, 3]. 20BaO·10Fe₂O₃·xMnO₂·(70-x)V₂O₅ glass showed a marked increase in σ after isothermal annealing at temperatures higher than T_g or T_c [4]. Mössbauer spectra of semiconducting LiFeVPO_x glass used as a cathode active material of lithium ion battery (LIB) evidently showed a reduction of Fe^{III} to Fe^{II} during the discharge as a result of an interaction of Li⁺ ions, and also a reverse oxidation from Fe^{II} to Fe^{III} during the charge as a result of deintercalation of Li⁺ ions [5]. It is expected that semiconducting vanadate glass containing Li⁺ would be an excellent cathode active material for LIB. Vanadate glass is known to have relatively low chemical durability, and hence it is important to improve the durability when applied to the cathode active material of LIB. Recent studies proved that semiconducting 20BaO·10Fe₂O₃·xWO₃·(70-x)V₂O₅ glass exhibited high electrical conductivity and high chemical or water durability [6, 7]. In this study, a relationship between the local structure and physical properties of WO₃-substituted lithium iron vanadate glass was investigated by means of ⁵⁷Fe-Mössbauer spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), differential thermal analysis (DTA), DC two- and four-probe measurements and a leaching test in 20 vol% HCl.

2 Experimental

20Li₂O·10Fe₂O₃·xWO₃·(70-x)V₂O₅ glasses, abbreviated as xLFWV, were prepared by a conventional melt-quenching method. Weighed amounts of Li₂CO₃, Fe₂O₃, WO₃ and V₂O₅ of reagent grade placed in a platinum crucible was melted at 1200 °C for 1 h in an electric muffle furnace. Homogeneous dark brown xLFWV glasses with 'x' less than 25 mol% were prepared when each melt was quenched by dipping the crucible bottom into ice-cold water. Enriched isotope of ⁵⁷Fe₂O₃ (95.54 %) was used for ⁵⁷Fe-Mössbauer measurement. Pulverized glass samples were used for isothermal annealing conducted at 400 °C for 100 min.

⁵⁷Fe-Mössbauer spectra were recorded at room temperature by a constant acceleration method. ⁵⁷Co(Rh) and α -Fe foil were used as a source and a reference of isomer shift (δ), respectively. FT-IR spectra were measured by KBr disk method in the region of 370 and 4000 cm⁻¹ under the resolution of 2 cm⁻¹. XRD was recorded with Cu-K α radiation ($\lambda = 1.54$ Å) between 2 θ of 10° and 80° with the

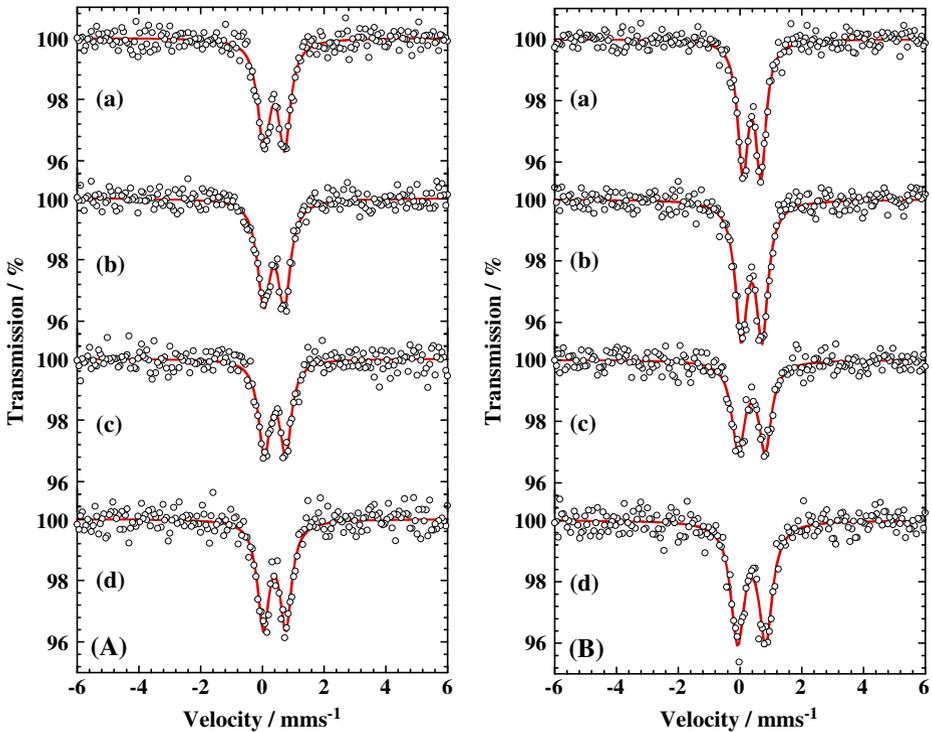


Fig. 1 ^{57}Fe -Mössbauer spectra of $x\text{LFWV}$ glasses with ‘ x ’ of (a) 0, (b) 10, (c) 20, (d) 25; (A) before and (B) after isothermal annealing at 400°C for 100 min

interval and scanning rate of 0.02° and 5°min^{-1} , respectively. DTA measurements were performed from RT and 700°C under N_2 gas atmosphere under heating rates of 5, 10, 15 and $25^\circ\text{C min}^{-1}$. Conductivity measurement was carried out from RT to 125°C by DC two- and four-probe method; the electrical current (I) was recorded by changing the voltage (V) between 1.0 and 10 V in the former case, whereas voltage (V) was recorded by changing the electrical current (I) between -1.0 and 1.0 mA in the latter. Value of σ ($\Omega^{-1}\text{cm}^{-1}$) was estimated using the following equation, *i.e.*,

$$\sigma = R^{-1} \cdot S^{-1} \cdot l, \quad (1)$$

where R , S and l are electrical resistance (in Ω) obtained from a slope of straight line of $V - I$ plot, surface area (in cm^2) and the distance between the electrodes (in cm), respectively. For the conductivity measurement, each glass sample was cut into a rectangular plate of which edges were coated with Ag solder to attach lead lines. Chemical durability was evaluated from the dissolution rate of each glass sample at RT measured after 72 h leaching test with ten-time weight of 20 vol% HCl solution.

3 Results and discussion

Mössbauer spectra of $x\text{LFWV}$ glasses measured before and after isothermal annealing at 400°C for 100 min are shown in Fig. 1. Before the annealing,

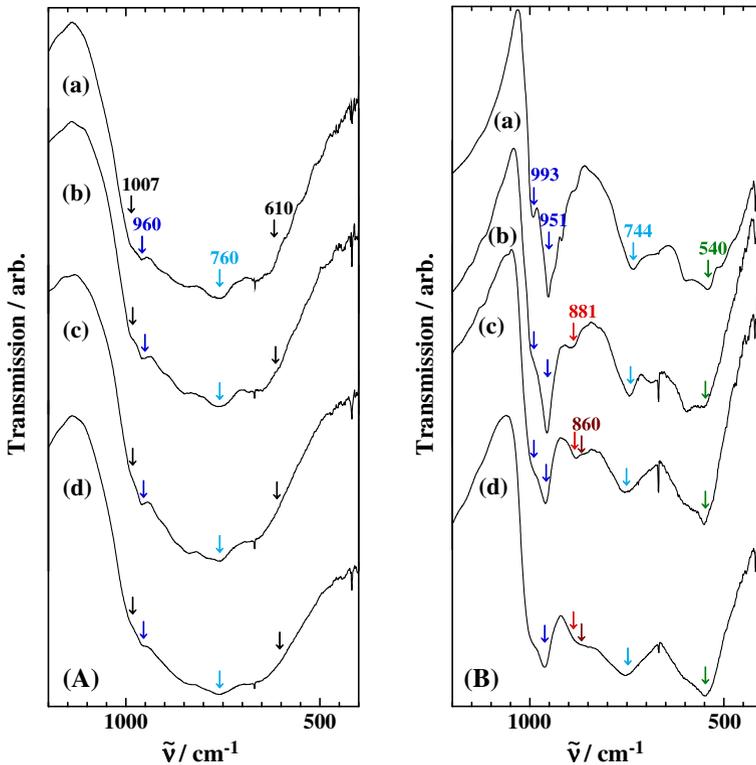


Fig. 2 FT-IR spectra of x LFWV glasses with ‘ x ’ of (a) 0, (b) 10, (c) 20, (d) 25; **(A)** before and **(B)** after annealing at 400 °C for 100 min

an identical δ of $0.39_{\pm 0.01}$ mm s⁻¹ and slightly increasing quadrupole splitting (Δ) value from 0.67 to 0.67, 0.69 and $0.73_{\pm 0.02}$ mm s⁻¹ were respectively observed with an increase of WO₃ content (x) from 0 to 10, 20 and 25 (see Fig. 1A(a–d)). This result indicates that local distortion of Fe^{III}O₄ tetrahedra was increased as a result of substitution of WO₃ for V₂O₅, as recently observed in 20BaO·10Fe₂O₃· x WO₃·(70– x)V₂O₅, 20Na₂O·10Fe₂O₃· x WO₃·(70– x)V₂O₅ and 20K₂O·10Fe₂O₃· x WO₃·(70– x)V₂O₅ glasses [7, 8].

After isothermal annealing at 400 °C for 100 min, smaller Δ of $0.58_{\pm 0.02}$ mm s⁻¹ was observed in x LFWV glass with ‘ x ’ of 0, reflecting the structural relaxation of tetrahedral FeO₄ and VO₄ units (see Fig. 1B(a)). In case of annealed x LFWV glasses with ‘ x ’ of 20 and 25 (Fig. 1B(c and d)), in contrast, larger Δ ’s of 0.87 and $0.91_{\pm 0.02}$ mm s⁻¹ were respectively observed, indicating that local distortion of FeO₄ and VO₄ units was increased when WO₃ substituted for V₂O₅. Similar increase in Δ was also observed in 20BaO·10Fe₂O₃· x WO₃·(70– x)V₂O₅, 20Na₂O·10Fe₂O₃· x WO₃·(70– x)V₂O₅ and 20K₂O·10Fe₂O₃· x WO₃·(70– x)V₂O₅ glasses with larger WO₃ content [7, 8]. These results indicate that structural relaxation of x LFWV glasses occurs at the sites of FeO₄ and VO₄, and not at the site of WO _{x} polyhedral.

FT-IR spectra of x LFWV glasses before and after annealing at 400 °C for 100 min are shown in Fig. 2. Before the annealing, a broad absorption band ranging from 610

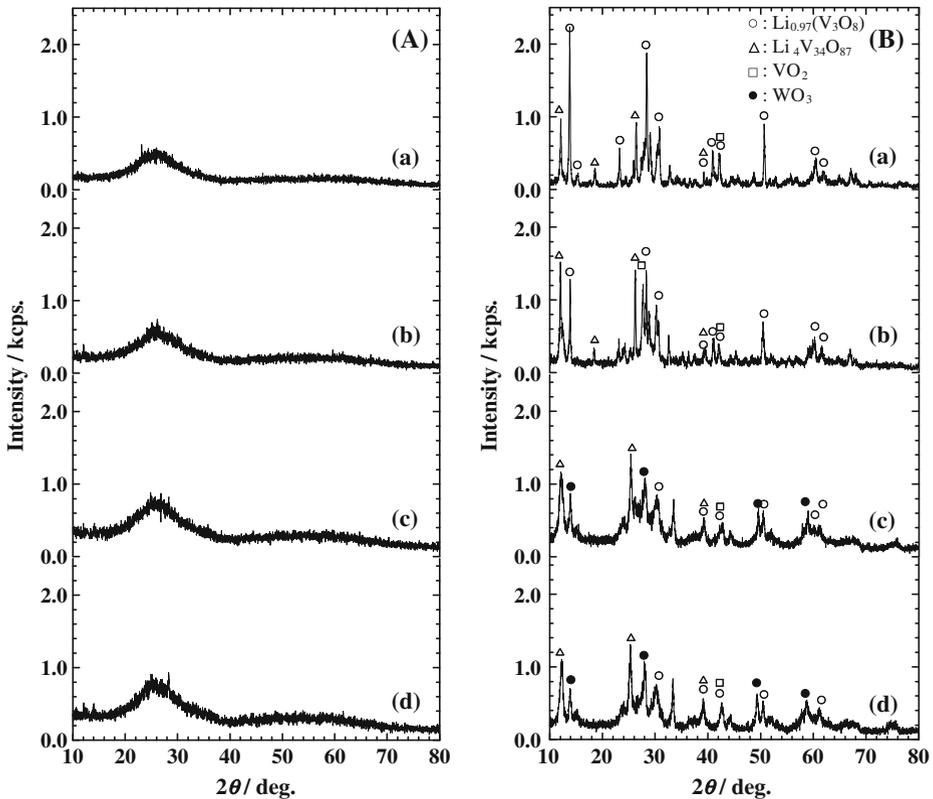
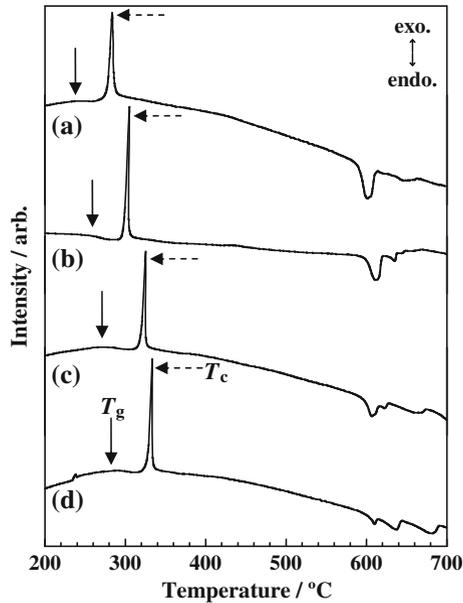


Fig. 3 XRD patterns of x LFWV glasses with ‘ x ’ of (a) 0, (b) 10, (c) 20, and (d) 25; (A) before and (B) after isothermal annealing at 400 °C for 100 min

to 1007 cm^{-1} was observed in each spectrum. It should be noted that the absorption band observed at 960 cm^{-1} attributed to V = O of VO_5 pyramid [9], and that at 760 cm^{-1} attributed to V-O of VO_4 tetrahedra [10] gradually decreased their intensity with an increase of WO_3 content. FT-IR spectrum of annealed x LFWV glass with ‘ x ’ of 0 (Fig. 2B(a)) showed sharp absorption bands at 993 and 951 cm^{-1} attributed to V = O of VO_5 pyramid, at 744 cm^{-1} attributed to V-O of tetrahedral VO_4 and at 540 cm^{-1} to Fe-O of tetrahedral FeO_4 units [11, 12]. In the FT-IR spectra of annealed x LFWV glasses with ‘ x ’ of 20 and 25 (Fig. 2B(c and d)), absorption bands observed at 881 cm^{-1} attributable to W-O bond of tetrahedral WO_4 [13] and that at 860 cm^{-1} to V-O bond of VO_5 pyramid [10] gradually increased the intensity with an increase of WO_3 content. These results evidently show that WO_4 and WO_6 units substituted for VO_4 and VO_5 units when WO_3 content (x) was increased in x LFWV glasses.

XRD patterns of x LFWV glasses with ‘ x ’ of 0, 10, 20 and 25 before and after annealing are shown in Fig. 3. Before annealing, one halo pattern characteristic of glass could be observed (see Fig. 3A(a–d)). After the annealing, several peaks were observed attributable to $\text{Li}_{0.97}(\text{V}_3\text{O}_8)$ ($2\theta = 13.7, 23.2, 28.3, 30.8$ and 50.8° ; PDF No. 01-073-8145), $\text{Li}_4\text{V}_{34}\text{O}_{87}$ ($2\theta = 12.1, 18.7$ and 26.3° ; PDF No. 00-046-0188) and VO_2 ($2\theta = 27.8$ and 42.3° ; PDF No. 01-082-0661) were observed in tungsten-free

Fig. 4 DTA curves of x LFWV glasses with ‘ x ’ of (a) 0, (b) 10, (c) 20 and (d) 25, measured under a heating rate of 5 Kmin^{-1}



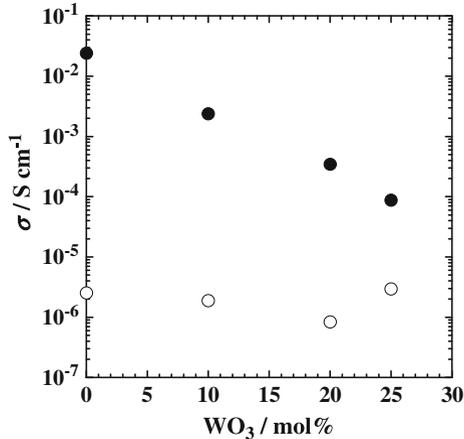
LFWV glass (Fig. 4B(a)). These results prove that crystalline phases containing V^{IV} and V^{V} were dominantly precipitated after the annealing of x LFWV glasses with small ‘ x ’ values. On the other hand, corresponding peaks were gradually decreased in annealed x LFWV glasses with ‘ x ’ of 20 and 25, while new peaks due to WO_3 ($2\theta = 14.1, 28.1, 49.1$ and 58.6° ; PDF No. 01-075-2187) were observed (see Fig. 4B(c and d)). Similar XRD patterns were also observed for $20\text{Na}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ and $20\text{K}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ glasses before and after annealing [8].

DTA curves of x LFWV glasses with ‘ x ’ of 0, 10, 20 and 25 recorded under a heating rate (α) of 5 Kmin^{-1} are depicted in Fig. 4. Values of T_g and T_c respectively increased from $252_{\pm 5}$ to 264, 284 and $298_{\pm 5}^\circ\text{C}$ and from $289_{\pm 3}$ to 310, 329 and 338°C with an increasing WO_3 content. A very simple linear relationship discovered between T_g and Δ , termed as T_g - Δ rule [14], is given by

$$T_g = a\Delta + b. \quad (2)$$

A large slope ‘ a ’ of $680 \text{ K}(\text{mm s}^{-1})^{-1}$ is generally yielded when Fe^{III} atoms occupy tetrahedral sites as network former (NWF), whereas it becomes only $35 \text{ K}(\text{mm s}^{-1})^{-1}$ when they occupy octahedral sites as network modifier (NWM). It is also known that the slope becomes $260 \text{ K}(\text{mms}^{-1})^{-1}$ when Fe^{III} atoms occupy octahedral NWF sites, as reported in sodium iron tungstate glasses [13]. In this study, T_g - Δ plot with 0.67 mm s^{-1} ($x=0$), 0.67 mm s^{-1} ($x=10$), 0.69 mm s^{-1} ($x=20$) and $0.73_{\pm 0.02} \text{ mm s}^{-1}$ ($x=25$) gave a straight line with a slope of $680 \text{ K}(\text{mms}^{-1})^{-1}$, indicating that Fe^{III} occupied ‘tetrahedral’ NWF sites, *i.e.*, substitutional sites of tetrahedral WO_4 units, as recently observed $20\text{BaO}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$, $20\text{Na}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ and $20\text{K}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ glasses [7, 8].

Fig. 5 Electrical conductivity (σ) of xLFWV glasses measured before (*open circle*) and after isothermal annealing at 400 °C for 100 min (*solid circle*)



Activation energy of crystallization (E_a) could be determined using Kissinger equation [15], *i.e.*,

$$\ln(T_c^2/a) = E_a/RT_c + \text{const.}, \quad (3)$$

where α and R are heating rate (K min^{-1}) and gas constant, respectively. As a result of Kissinger plot, E_a of 2.5, 2.5, 2.7 and 3.7 eV were respectively obtained for xLFWV glasses with ‘ x ’ of 0, 10, 20 and 25 mol%. It is known that binding energies of V-O, W-O and Fe-O bonds are 3.9–4.4, 4.5 and 2.6 eV, respectively [16]. Hence, we can speculate that crystallization of xLFWV glass is triggered by the cleavage of Fe-O bonds when ‘ x ’ is equal to or smaller than 20, and by the cleavage of V-O bonds when ‘ x ’ is 25, as likely to be observed for crystallization studies of $20\text{Na}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ and $20\text{K}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ glasses [8]. It is considered that the gradual increase in E_a is involved with the increase in T_g , T_c and Δ .

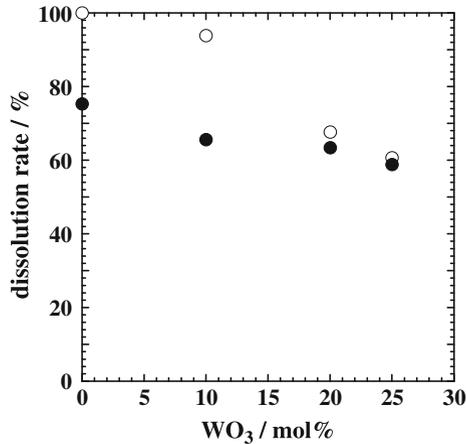
Figure 5 depicts that σ of xLFWV glasses with ‘ x ’ of 0, 10, 20 and 25 were 2.5×10^{-6} , 1.9×10^{-6} , 8.4×10^{-7} and 2.9×10^{-6} S cm^{-1} , respectively, which increased to 2.4×10^{-2} , 2.4×10^{-3} , 3.5×10^{-4} and 8.8×10^{-5} S cm^{-1} after isothermal annealing at 400 °C for 100 min. These results indicate that increase in σ caused by structural relaxation of glass network is not related to “tungstate glass”, but is intrinsic of “vanadate glass”. Increase in σ was also observed in $20\text{Na}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ and $20\text{K}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ glasses before and after annealing [8].

Activation energy of electrical conduction (W_H) could be calculated using the following equation [17], *i.e.*,

$$\ln \sigma T = \ln \sigma_0 - W_H/kT, \quad (4)$$

where T , σ_0 and k are measurement temperature (in K), conductivity at given temperature and Boltzmann constant, respectively. W_H values of $0.33_{\pm 0.04}$ ($x = 0$), $0.32_{\pm 0.02}$ ($x = 10$) and $0.39_{\pm 0.06}$ ($x = 20$) eV were obtained in xLFWV glasses, which respectively decreased to $0.10_{\pm 0.01}$, $0.12_{\pm 0.02}$ and $0.16_{\pm 0.01}$ eV after the annealing. These results suggest that W_H decreases by the structural relaxation, which causes

Fig. 6 Dissolution rate of x LFWV glasses with different WO_3 content before (*open circle*) and after annealing at 400°C for 100 min (*solid circle*), evaluated from the leaching test with 20 vol% HCl



a marked increase in σ , as observed in LiFeVPO_x and other vanadate glasses after isothermal annealing [2–8].

In Fig. 6 is plotted dissolution rate of x LFWV glasses after 72 h-leaching test in 20 vol% HCl. Before annealing, dissolution rates of x LFWV glasses with “ x ” of 0, 10, 20 and 25 were 100, 93.8, 67.7 and 60.7 %, respectively (open circle). In contrast, smaller dissolution rates of 75.3, 65.6, 63.4 and 58.8 % were estimated in corresponding x LFWV glasses after annealing (solid circle), indicating that isothermal annealing of x LFWV glasses at 400°C for 100 min causes an advanced chemical durability. It is concluded that chemical properties of x LFWV glasses could be controlled by changing WO_3 content.

4 Summary

A relationship between local structure and physical property of $20\text{Li}_2\text{O}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$ glass was investigated. From the Mössbauer and DTA studies, it was revealed that Fe^{III} occupied tetrahedral NWF sites. A marked increase in σ and a decrease in the dissolution rate was observed after isothermal annealing at 400°C for 100 min when ‘ x ’ was 10, suggesting that introduction of WO_3 into vanadate glass causes an enhancement of chemical durability without a remarkable loss of the electrical conductivity. It is expected that Li_2O - and WO_3 -containing vanadate glass might be utilized as excellent cathode active material for LIB.

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