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Development of Electrically Conductive ZrO2-CaO-Fe2O3-V2O5 Glass and Glass-Ceramics as a New Cathode Active Material for Na-ion Batteries with High Performance

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1 **Development of Electrically Conductive ZrO$_2$-CaO-**

2 **Fe$_2$O$_3$-V$_2$O$_5$ Glass and Glass-Ceramics as a New Cathode**

3 **Active Material for Na-ion Batteries with High**

4 **Performance**

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1 **Abstract**

2 Glass-ceramics xZrO$_2$•10Fe$_2$O$_3$•(90-x)V$_2$O$_5$ with 'x' between 0 and 30 mol% and

3 yZrO$_2$·(20-y)CaO·10Fe$_2$O$_3$·70V$_2$O$_5$ glass with 'y' between 0 and 20 mol%,

4 respectively abbreviated as xZFV and yZCFV, before and after heat treatment at

5 500 °C for 100 min, were evaluated as potential cathode-active materials for

6 sodium-ion batteries (SIBs). Relationships between physical properties and local

7 structure of xZFV and yZCFV glass-ceramics were investigated by [57]Fe-

8 Mössbauer spectroscopy, V K-edge X-ray absorption near edge structure

9 (XANES), X-ray diffractometry (XRD), DC four-probe method and differential

10 thermal analysis (DTA). SIBs containing heat-treated xZFV glass-ceramics

11 showed the highest discharge capacity of 153 mAh•g^{-1} under a current density of

12 50 mA•g^{-1}, which exhibited a high electrical conductivity of 1.8×10^{-2} Scm^{-1}.

13 Precipitation of V$_{0.05}$Zr$_{0.95}$O$_2$ and Fe$_2$V$_4$O$_{13}$ nanoparticles were confirmed from the

14 XRD pattern of the heat-treated 20ZFV glass, consistent with the lower energy of

15 the pre-edge peak at 5467 eV in the V K-edge XANES spectrum. This result is

16 associated with the reduction of vanadium ions from V^{V} to V^{IV}. It is concluded

17 that the precipitation of stable vanadium bronze phases with high electrical

18 conductivity and structural stability effectively enable the high SIB capacity of

19 these materials.

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21 **Keywords** Na-ion battery, vanadate glass, [57]Fe-Mössbauer spectroscopy, XAFS

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1. Introduction

Lithium-ion batteries (LIB) are widely utilized as a secondary battery for electrical facilities such as laptop PCs and smartphones because of the high theoretical capacity of 3861 mAh g^{-1}[1]. However, the small abundance of Li in the Earth's crust (0.006) will cause future scarcity and an increase in the price of LIB [1]. Therefore, post-lithium-ion batteries with the large capacity and long lifetime have been keenly investigated. Among these, sodium-ion batteries (SIB) are strong candidates for post-lithium-ion batteries because of the high availability of sodium, having a larger abundance in the Earth's crust of 2.63 and a high theoretical capacity of 1166 mAh•g^{-1} next to LIB [1-3]. Many researchers have investigated SIB with high performances. For example, Yasin *et al.* successfully prepared SIB with the capacity of 122 mAh•g^{-1} maintained after 4000 cycles by using graphene as the anode [4], which leads to an oxygen reduction catalyst [5]. Concerning the development of new cathode active materials for SIB, $30Na_2O•40FeO•30P_2O_5$ glass exhibited an initial discharge capacity of 115 mAh •g^{-1} when it was incorporated as a cathode active material of SIB[6]. In addition, NASICON-type $Na_3V_2(PO_4)_3$ nanoparticles prepared by an electrospinning method as a cathode of SIB showed a larger initial discharge capacity of 94 mAh •g^{-1} than that of the bulk material of 56 mAh•g^{-1} [7]. Furthermore, Uchaker *et al.* reported that amorphous V_2O_5 prepared by a combination of sol-gel method and electrochemical deposition showed a capacity of 241 mAh•g^{-1} [8]. These previous studies indicate that amorphous vanadates present high potentially novel opportunities for utilizing a new cathode active material for SIB.

Vanadate glasses and glass-ceramics are known semiconductors, with electrical conductivities (σ) of 10^{-7}-10^{-5} S cm^{-1}, attributed to $3d$ electron (polaron) hopping from V^{VI} or V^{III} to V^{V} [9, 10]. It has been reported that a drastic increase in the electrical conductivity (σ) from 10^{-7} to 10^{0} S cm^{-1} took place in semiconducting barium iron vanadate glass, *e.g.*, $20BaO•10Fe_2O_3•70V_2O_5$ glass, when it was heat-treated at temperatures higher than glass transition temperature (T_g) or crystallization temperature (T_c) [11, 12], thus forming a glass-ceramic. Furthermore, Kubuki reported that the σ value of alkaline iron vanadate glass (R_2O-V_2O_5-Fe_2O_3, R: Li, Na) was sensitively affected by the crystalline phase precipitated in the glass system [13]. For example, $20Na_2O•70V_2O_5•10Fe_2O_3$ glasses showed the largest σ of 2.5×10^{-2} S cm^{-1} after heat treatment at 500 ℃ for

1   100 min, but a decrease in σ was observed when heat-treated at 550 $^{\circ}$C for 100

2   min due to the precipitation of $FeVO_4$ having the smaller σ of 4.7×10^{-5} S cm^{-1}

3   [14]. These results show that σ of vanadate glass can be regulated by the heat-

4   treatment temperature and the glass composition.

5   This unique electrical "tuneability" of vanadate glass / glass-ceramics could

6   enable their application as an electrode of secondary batteries. Kubuki *et al.*

7   revealed that heat-treated $15Li_2O \bullet 10Fe_2O_3 \bullet 20SnO_2 \bullet 5P_2O_5 \bullet 50V_2O_5$ glass resulted

8   in a remarkable increase in σ amounting to the order of 10^{-2} S cm^{-1} and a large

9   capacity of 493 mAh$\bullet$g^{-1} when incorporated into the cathode of LIB [15, 16].

10 For the expected Li scarcity in the future, they also prepared a new vanadate glass

11 as a cathode active material of SIB as a post-lithium-ion battery. Kubuki

12 reported that the cathode-active materials of $xNa_2O \bullet (90-x)V_2O_5 \bullet 10P_2O_5$ glass with

13 '*x*' of 5, 25 and 45 mol%, provided a relatively high discharge capacity of 150–

14 200 mAh$\bullet$g^{-1} after recycling of 5 times under the voltage between 0.8 and 3.6 V

15 with the current density of 0.2 mA cm^{-2}[17]. The improvement of capacity and

16 cycle stability of SIB are recent focuses of a new vanadate glass as the high-

17 performance cathode. High conductivity, chemical and thermal stabilities are

18 essential factors for achieving this goal. Compared with the *x*NPV glass,

19 increase of stability is expected when Na$^+$ is substituted for other cations with

20 high valence states such as Ca^{2+} and Zr^{4+} because CaO-ZrO$_2$ ceramics is known as

21 an ion conductor.

22 In order to develop new vanadate glasses and glass-ceramics with high

23 electrical conductivity and structural stability, favourable for cathode active

24 materials for SIBs with high capacities, a relationship between the local structure

25 and physical properties of glass-ceramics systems ZrO_2-V_2O_5-Fe_2O_3 and CaO-

26 ZrO_2-V_2O_5-Fe_2O_3 were investigated by ^{57}Fe-Mössbauer spectroscopy, XANES,

27 XRD, Ultraviolet-Visible (UV-Vis) absorption spectroscopy, diffuse reflectance

28 spectroscopy (DRS) and DC four-probe method together with a charge-discharge

29 capacity measurement of the SIB.

30

31 **2. Experimental**

32 New vanadate glass and glass-ceramics with the nominal composition of

33 $xZrO_2 \bullet 10Fe_2O_3 \bullet (90-x)V_2O_5$ (*x*=0-30 in mol %) and $yZrO_2 \bullet (20-$

1 y)CaO•10Fe$_2$O$_3$•70V$_2$O$_5$ glasses (y=0-20 in mol%), respectively abbreviated as

2 xZFV and yZCFV, were prepared by a conventional melt-quenching method.

3 Weighed amounts of reagent-grade ZrO$_2$ (Wako:264-00485), CaCO$_3$ (Wako:030-

4 00385), Fe$_2$O$_3$ (Wako:096-04825) and V$_2$O$_5$ (Wako:225-00125) were well mixed

5 in an agate mortar, and the mixture in a platinum crucible was melted at 1200 ^{o}C

6 for 1 h in an electric muffle furnace.   Homogeneous black samples of xZFV and

7 yZCFV glasses were obtained by dipping the crucible bottom into ice-cold water.

8 The well-pulverized samples were heat-treated in platinum crucibles at 500 ^{o}C for

9 100 min in air.   For ^{57}Fe-Mössbauer measurement, an enriched isotope of

10 ^{57}Fe$_2$O$_3$ (95.54%) was used for the sample preparation.

11   Measurements of differential thermal analysis (DTA) were performed from

12 room temperature (RT) to 700 ^{o}C under the heating rate (α) of 10 K•min^{-1} using

13 Themo plus TG8120 (Rigaku).   Ten milligrams of well-pulverized samples and a

14 reference of α-Al$_2$O$_3$ powder were used for the measurements. For estimating

15 activation energy for crystallization (E_a), the Kissinger equation [18] was applied,

16 *i.e.*,

17

18 $$\ln (T_c^2 / \alpha) =\ \ E_a/RT_c + C \tag{1},$$

19

20   where T_c, R and C are crystallization (peak) temperature, gas constant, and

21 constant, respectively.   Electrical conductivity was measured from RT to 125 ^{o}C

22 by DC four-probe method using DC Voltage Current Source Monitor (6241A,

23 ADC).   The sample connection in the circuit is indicated in Figure 1.   The

24 electrical voltage (E) was recorded by changing the electrical current (I) between -

25 10 and 10 mA. By attaching electrodes separatory to an ammeter and voltmeter,

26 the resistance of voltmeter is cancelled.   Therefore, a more precise evaluation is

27 achieved as compared with DC-two probe method.

28   The value of σ (Ω^{-1}•cm^{-1}) was estimated using the following equation, *i.e.,*

29

30 $$\sigma\ \ = R_s^{\ -1} \bullet S^{-1} \bullet l \tag{2},$$

31

32 where R_s, S and l are electrical resistivity (in Ω) obtained from a slope of a

33 straight line of E *vs.* I plot, surface area (in cm^2) and the distance between the

electrodes (in cm), respectively.   For conductivity measurements, each glass block sample was ground into a rectangular plate of which edges were coated with Ag solder to attach lead lines.   By using a RINT-TTR III (Rigaku) X-ray diffractometer, XRD patterns were recorded using Cu-K$_\alpha$ radiation (λ = 1.54 Å) between 2Θ of 10° and 80° with data interval and scanning rate of 0.02° and 5° min^{-1}, respectively.   The obtained XRD patterns were analyzed by PDXL2 (Rigaku) software with the database of ICDD PDF4 (Light Stone). Surface observation of the prepared samples using scanning electron microscopy (SEM) was performed by VE-9800 (Keyence) under the applied voltage of 2 kV with a magnitude of 5×10^3.   X-ray absorption spectra at the vanadium K-edge using synchrotron radiation were measured at room temperature at beamline BL11 of the Saga Light Source (Yayoigaoka 8-7, Tosu, Saga 841-0005, JAPAN) using a double Si (111) monochromator.   The thickness of the samples was controlled to enable transmission mode measurement (V K-edge).   [57]Fe-Mössbauer spectra were recorded at room temperature by a constant acceleration method.   The system was composed of a driving unit (MDU-1200, Wissel), a digital function generator (DFG-1000, Wissel), a proportion counter (4546, Niki Kogei), a preamplifier (142IH, ORTEC), a high voltage supply (456, ORTEC), an amplifier (485, ORTEC) and a multichannel analyzer (EASY-MCS, ORTEC).   A [57]Co (Rh) source with the radioactivity of 925 MBq (MCo7. 123, produced on Jan. 10, 2018, by Ritverc) and α-Fe foil were used as a source and a reference of isomer shift (δ), respectively.   Obtained spectra were analyzed by Mosswinn4.0 with Lorentzian fitting.   The optical bandgap was estimated from diffuse reflectance UV-Vis spectroscopy recorded on Shimadzu UV-3600 spectrometer with an integrating sphere attachment (ISR-3100, Shimadzu).   Estimation of optical band gap was carried out by diffuse reflectance UV-Vis spectroscopy and using the Kubelka–Munk equation [19]:

$$F(R_\text{f}) \quad = \quad (1\text{-}R_\text{f})^2 \bullet (2R_\text{f})^{-1} \hspace{3cm} (3),$$

where R_f is the reflectance.   Further information was obtained by the Tauc plots [20]:

1      $$\alpha \bullet h \bullet \nu \ = \ A \bullet (h\nu - E_g)^n \hspace{4cm} (4),$$

2

3   where A is the proportionality constant, α is the absorption coefficient (here, $F(R)$

4   being directly proportional to α), ν is the frequency of light and E_g is the bandgap.

5   The value of n is dependent on the nature of the transition: n is 1/2 for a directly

6   allowed transition and 2 for an indirectly allowed transition [21, 22]. Sodium-

7   ion battery (SIBs) were prepared in 2032 type containing the anode of metallic Na

8   (Kishida: 620-70852), the electrolyte of $NaClO_4$ / propylene carbonate solution

9   (Tomypure: LIPASTE-P/S1), and the cathode with the ratio of sample: acetylene

10 black (AB, Strem chemicals: 06-0025): polytetrafluoroethylene (PTFE, Wako:

11 165-13412) of 70:25:5. The cathode and anode were respectively loaded by 30

12 and 90 mg, where each electrode had a 1cm diameter. An ECD8-0.5-LUs1

13 (Matsusada Precision) measured the charge-discharge capacity performance by

14 repeating 30 times under the voltage window of 0.8-3.6V, a current density of 50

15 mA g^{-1} (=2.0 mA cm^{-2}), and the cut-off current of 0.5 mA in the charging process

16 under CCCV mode.

17

18 **3. Results and Discussion**

19   DTA curves of xZFV and yZCFV samples are depicted in Figure 2. In the

20 case of xZFV glass, T_g and T_c respectively varied from $244_{\pm 5}$ to $250_{\pm 5}$, $250_{\pm 5}$, and

21 $251_{\pm 5}$ ^oC, and from $324_{\pm 2}$ to $360_{\pm 2}$, $350_{\pm 2}$ and $361_{\pm 2}$ ^oC with ZrO_2 concentration

22 (x). On the other hand, a decrease in T_g from 284 to 250 ^oC and T_c from 387 to

23 350 ^oC were observed for yZCFV with ZrO_2 concentration (y). Decreases in T_g

24 and T_c observed for yZCFV imply that thermal durability was decreased when

25 Zr^{4+} was replaced by Ca^{2+} because the network forming cation of vanadium is

26 partially reduced from V^{5+} to V^{4+}. On the contrary, the role of Zr^{4+} in the glass

27 network of xZFV is not clear due to the high oxidation number of 4+. Based on

28 the T_g's and T_c's of xZFV and yZCFV glasses, the isothermal annealing was

29 conducted at 500 ^oC for 100 min. From the Kissinger plot, E_a's were calculated

30 to be $2.6_{\pm 0.3}$, $2.6_{\pm 0.2}$, $2.7_{\pm 0.1}$ and $2.6_{\pm 0.3}$ eV for xZFV glass with 'x' of 0, 10, 20 and

31 30, while $2.2_{\pm 0.8}$, $3.2_{\pm 0.4}$, $2.9_{\pm 0.5}$, $2.7_{\pm 0.2}$ and $2.7_{\pm 0.1}$ eV for yZCFV glass with y of 0,

32 5, 10, 15 and 20. Because chemical bond energies were reported to be 2.6 eV for

1   Fe^{III}-O and 3.9-4.9 eV for V-O[23], this result implies that only the Fe-O chemical

2   bond was cleaved and rearranged during the crystallization.

3   In Fig. 3, electrical conductivity (σ) and activation energy of electrical

4   conduction (W_H) of xZFV glass were plotted against ZrO$_2$ content before and after

5   heat treatment at 500 $^{\circ}$C for 100 min.   Before the heat treatment, a gradual

6   increase in σ was observed from 6.3$\times10^{-5}$ to 2.9$\times10^{-4}$, 1.6$\times10^{-3}$ and 2.9$\times10^{-3}$ S cm^{-}

7   ^{1} with an increase of ZrO$_2$ content in xZFV glass from 0, 10, 20 and 30 mol%,

8   respectively (Fig.3 (A)(a)).   The activation energy of electrical conduction (W_H)

9   was calculated using the following equation [24], *i.e.*,

10

11          $\ln\sigma T$ = $\ln\sigma_0 - W_H / kT$ (5),

12

13   where T, σ_0 and k are measurement temperature (in K), conductivity at a given

14   temperature,   and   Boltzmann   constant   (1.380$\times10^{-23}$ JK^{-1}).   By   measuring

15   electrical conductivity under different temperatures, required energy for moving

16   carries, *i.e.* W_H, can be estimated as a slope of a straight line with the intercept of

17   $\ln\sigma_0$.   Gradual decreases in W_H's from 0.18$_{\pm0.01}$ (x=0) to 0.16$_{\pm0.02}$ (x=10), 0.15$_{\pm0.02}$

18   (x=20) and 0.13$_{\pm0.01}$ (x=30) eV, and from 0.16$_{\pm0.02}$ (x=0) to 0.15$_{\pm0.02}$ (x=10),

19   0.15$_{\pm0.02}$ (x=20) and 0.14$_{\pm0.02}$ (x=30) were observed before and after heat treatment,

20   respectively.   These results indicate that the probability of electron hopping was

21   increased by substituting ZrO$_2$ for V$_2$O$_5$ in xZFV glass, regardless of the heat

22   treatment.   It is considered that the increase of σ in xZFV glass before and after

23   the heat treatment is caused by the reduction of vanadium with ZrO$_2$ content.   In

24   Fig. 4, σ and W_H of yZCFV glass were plotted against ZrO$_2$ content before and

25   after heat treatment at 500 $^{\circ}$C for 100 min.   As shown in open circles in Fig. 4

26   (A), σ of yZCFV glass before the heat treatment was increased from 3.7$\times10^{-6}$ to

27   1.6$\times10^{-3}$ S cm^{-1} with ZrO$_2$ content because of the reduction of vanadium ion from

28   V^V to V^{IV}.   As for heat-treated yZCFV glass, σ decreased from 6.7$\times10^{-1}$ to

29   1.8$\times10^{-2}$ S cm^{-1}, while W_H increased from 0.09 to 0.15 eV with ZrO$_2$

30   concentration.   It is noted that σ dramatically increased from 3.7$\times10^{-6}$ to 6.7$\times10^{-}$

31   ^{1} S cm^{-1} when 0ZCFV glass was heat-treated at 500 $^{\circ}$C for 100 min, while

32   differences in σ between before and after heat treatment become smaller in the

33   case of yZCFV with 'y' of larger than 5 mol%.

XRD patterns of xZFV glass with 'x' of 0, 10, 20 and 30 recorded before the heat treatment are shown in Fig. 5.   A halo pattern was observed for xZFV glass with 'x' of 0 and 10, indicating the presence of an amorphous structure in the glass matrix as shown in Fig. 5 (a)-(b).   On the other hand, a halo pattern superimposed by intense sharp peaks attributed to crystalline phases of $V_{0.03}Zn_{0.97}O_2$ (PDF No. 01-072-6680, open circles) and weak sharp peaks attributed to crystalline V_2O_5 (PDF No. 01-089-2482, solid circles) and VO_2 (PDF No. 03-065-7960, solid rhombuses) were also observed for samples 20ZFV and 30ZFV (see Fig. 5 (c)-(d)).   The crystalline phase of $V_{0.03}Zn_{0.97}O_2$ was unexpectedly produced because a clear surface was observed for as-quenched 20ZFV glass.   Peaks attributed to V_2O_5 were disappeared with increasing 'x' from 20 to 30, while those due to VO_2 appeared, suggesting that V^V was partially reduced into V^{IV} with increasing ZrO_2 content in xZFV glass. $V_xZr_{1-x}O_2$ called "vanadium-zirconia yellow baddeleyite", is a well-known ceramic pigment. The oxidation number 4+ in vanadium was found in both solid solutions (monoclinic and tetragonal) based on zirconia crystalline forms [25-27].   Hence, the presence of the crystalline phase of $V_xZr_{1-x}O_2$ ($0 \leq x \leq 0.1$) could be evidential to conclude that V_2O_5 was reduced to VO_2 during sample preparation.   XRD patterns for 20ZFV and 0ZCFV glass samples before and after the heat treatment are illustrated in Fig. 6.   The XRD pattern for sample 20ZFV before the heat-treatment was mentioned in the previous section, while crystalline phases of $V_{0.05}Zr_{0.95}O_2$ (PDF No. 01-072-6681: double circles) and $Fe_2V_4O_{13}$ (PDF No. 01-089-5460: solid triangles) were detected in the heat-treated sample.   Precipitation of $V_{0.05}Zr_{0.95}O_2$ phase observed for heat-treated 20ZFV shows that the fraction of V^{IV} is increased. The XRD pattern for sample 0ZCFV showed a halo pattern characteristic of glass amorphous structure, whereas some sharp intense peaks attributed to $Ca_{0.17}V_2O_5$ (PDF No. 00-026-1165: open triangles), CaV_2O_6 (PDF No. 01-073-0186: open squares), $FeVO_4$ (PDF No. 00-038-1372: open rhombuses) and V_2O_5 were observed for the heat-treated samples (see Fig. 6(B) (a)-(b)).   The crystalline phase $Ca_{0.17}V_2O_5$ is called beta-vanadium bronze (β-$M_xV_2O_5$), a highly conductive anisotropic semiconductor with σ of 10^0-10^1 S cm^{-1} at room temperature due to small polaron hopping [28-33].   It was reported that highly conductive glass-ceramics containing vanadium bronze could be produced through the crystallization of vanadate glasses.   Hirashima et $al.$ reported that the

9

1   DC conductivity of the crystallized Na_2O-V_2O_5-P_2O_5 glasses was more than 3

2   orders of magnitude higher than that of as-cast glasses [34].   A drastic increase

3   in conductivity observed here for 0ZCFV glass after heat treatment is associated

4   with the precipitation of vanadium bronze. Considering the difference of σ values

5   between 20ZFV and 0CZFV glasses, the network modifier (Ca^{2+}, in this study)

6   seems to have played a significant role in forming the vanadium bronze ($M_xV_2O_5$)

7   phase.

8   In Figure 7, SEM images of 20ZFV and 0CZFV are indicated. We could

9   confirm a crystalline of $Zr_{0.03}V_{0.97}O_2$ with the particle size of about 50 μm in

10 20ZFV before treatment (Fig. 7 (A-a)), while rod-like crystalline of $Zr_{0.05}V_{0.95}O_2$

11 and $Fe_2V_4O_{13}$ with the length of 20 μm were found in heat-treated sample

12 20ZFV(Fig. 7 (A-b)).   Clear surface without crystalline phases is observed from

13 SEM image of 0ZCFV glass (Fig. 7 (B-a)), while small particles with the size of

14 smaller than 2 μm were found in heat-treated 0ZCFV(Fig. 7 (B-b)).

15   To help determine the oxidation states of vanadium in these materials, V K-

16 edge XANES measurements were performed on the xZFV and yZCFV glasses.

17 Fig. 8 (A) shows the normalized V K-edge spectra of xZFV glass measured before

18 heat treatment, together with spectra for V_2O_5, VO_2 and V_2O_3 chemical reagents.

19 The V K pre-edge peaks for xZFV glasses with 'x' of 0, 10, 20 and 30 were

20 observed at 5466.9, 5466.6, 5467.0 and 5466.6 eV with the normalized intensity

21 of 0.298, 0.311, 0.291 and 0.258, respectively.   On the other hand, the V K pre-

22 edge peaks for the references of V_2O_5, VO_2, and V_2O_3 were respectively observed

23 at 5467.3, 5466.4, 5467.3 eV with the normalized intensity of 0.276, 0.073 and

24 0.054, respectively.   The pre-edge peak has been attributed to a $1s$-$3d$ electronic

25 transition [35].   The intensity of the V K-pre-edge peak exhibited little change

26 with increasing ZrO_2 content, except for a small decrease in intensity with the

27 highest ZrO_2 content ($x = 30$) (Fig. 8(A)(d)).   As reported previously on different

28 vanadium-bearing compounds, the pre-edge peak intensity of V K-edge XANES

29 spectra shifts toward the smaller intensity when the average oxidation state of

30 vanadium decreases [36-38].   However, in addition, the pre-edge peak intensity

31 (herein estimated from peak height and not the integrated peak area) is also

32 strongly affected by the symmetry of V-O_x polyhedra, as discussed in depth by

33 [35-37]. Consequently, the pre-edge peak intensity from V K-edge XANES

34 spectra is a convolution of the effects of oxidation state and site symmetry

1   (coordination).   As discussed by [36, 37], these relationships are distinctly non-

2   linear and thus are challenging to deconvolute. Consequently, we can conclude

3   here that the combined effects of (oxidation state and site symmetry) were

4   approximately the same for xZFV glasses when $x = 0$, 10 and 20; and that one or

5   both of (i) average oxidation state decreased slightly; and / or (ii) average

6   coordination number increased slightly, when x increased to 30 in this glass

7   system. The V K-edge XANES pre-edge peak data for 20ZFV and 0ZCFV glasses

8   were also similar to each other, both before and after heat treatment (Fig. 9 (A)

9   and (B)).   A slight decrease in the normalized intensity of sample 0ZCFV before

10 and after heat treatment was observed from 0.320 to 0.303, while the constant

11 normalized intensity of 0.291 was observed for heat-treated sample 20ZFV. This

12 again suggests only small changes in average (oxidation state / coordination

13 number) between these four samples. However, there are some subtle differences

14 between the spectra: the spectra for the two heat-treated samples exhibited

15 narrower linewidths, consistent with a narrower range of site parameters (thus

16 with crystallization). In addition, a weak shoulder at approximately 5464.5 eV is

17 resolved in these two spectra, indicating a contribution from VO_2, $i.e.$ confirming

18 the presence of V^{4+}.   Indeed, the normalized V-K pre-edge peak intensity did not

19 change between before and after the heat-treatment of xZFV glass, although that

20 of 0ZCFV glass was slightly decreased after the heat treatment (Fig. 9 (B)).   We

21 can thus conclude that the oxidation state and average coordination of vanadium

22 in all glasses studied were similar, and that heat treatment of the two glasses to

23 form glass-ceramics, also resulted in little difference in the pre-edge peak height,

24 reflecting little change in the average vanadium (oxidation state / coordination).

25   Mössbauer spectra and the parameters of the xZFV glasses measured before

26 and after heat treatment at 500 $^{\circ}$C for 100 min are shown in Fig. 10 and Table 1.

27 Before heat treatment, Fe ions were homogeneously distributed in the glass matrix

28 because no crystalline phases containing Fe were identified by the corresponding

29 XRD patterns (see Fig. 5).   An identical δ of $0.39_{\pm0.01}$ mm s^{-1} and closely similar

30 quadrupole splitting (Δ) from 0.67 to 0.68, 0.74 and $0.72_{\pm0.02}$ mm s^{-1} were obtained

31 by fitting spectra, with an increasing ZrO_2 content (x) from 0 to 10, 20 and 30 (see

32 Fig. 10 (A)(a)-(d)), respectively.   This result indicates that local distortion of

33 $Fe^{III}O_4$ tetrahedra [39] was slightly increased as a result of the substitution of ZrO_2

34 for V_2O_5, as previously observed in $20BaO \cdot 10Fe_2O_3 \cdot xWO_3 \cdot (70-x)V_2O_5$ and

1     $20R_2O \cdot 10Fe_2O_3 \cdot xWO_3 \cdot (70−x)V_2O_5$ (R = Na, K) glasses [40, 41]. Two doublets

2   with isomer shift (δ) and quadrupole splitting (Δ) of $0.38_{\pm 0.01}$ and $0.29_{\pm 0.02}$ mm s^{-1},

3     $0.30_{\pm 0.03}$ and $1.29_{\pm 0.07}$ mm s^{-1} were observed in ^{57}Fe-Mössbauer spectra of the

4   heat-treated xZFV glass samples, respectively of which is ascribed to a crystalline

5     $Fe^{III}_2V^V_4O_{13}$ and an amorphous Fe^{III}-V^{IV}-O phase [42] (Fig. 10 (B)(a)-(d)). ^{57}Fe-

6   Mössbauer spectra and the parameters of yZCFV glass with 'y' of 0, 5, 10, and 15

7   mol% before and after heat treatment at 500 ^{o}C for 100 min are shown in Fig. 11

8   and Table 2.   Before the heat treatment, an identical δ of $0.38_{\pm 0.01}$ mm s^{-1} and

9   almost identical Δ values of 0.76, to 0.77, 0.75, and $0.74_{\pm 0.02}$ mm s^{-1} were

10   respectively observed with an increase in ZrO_2 content (y) from 0 to 5, 10 and 15

11   (see Fig. 11 (A)(a)-(d)).   This result shows that the local distortion of tetrahedral

12     $Fe^{III}O_4$ was not affected by ZrO_2.   This is the case for "distorted" VO_x polyhedra

13   since they are directly connected to the "distorted" FeO_4 tetrahedra by sharing

14   corner oxygen atoms.   Since high-spin Fe^{III} has an isotropic electron

15   configuration of 3d^5, the *electric field gradient (EFG)* caused by valence electrons

16   (eq_{val}) is "zero".   Therefore, Δ reflects the *EFG* caused by the distortion of lattice

17   (eq_{lat}), *i.e.*, composed of $Fe^{III}O_4$ and VO_x polyhedra.   It is expected that the

18   probability of electron hopping from V^{VI} or V^{III} to V^V will be enhanced by

19   substituting ZrO_2 for CaO.   On the contrary, three paramagnetic doublets which

20   are ascribed to $Fe^{III}V^VO_4$ [13, 42] with δ and Δ of $0.39_{\pm 0.01}$ and $0.65_{\pm 0.02}$, $0.39_{\pm 0.01}$

21   and $0.33_{\pm 0.02}$, and $0.32_{\pm 0.01}$ and $1.12_{\pm 0.02}$ mm s^{-1} were observed from heat-treated

22   0ZCFV glass (Fig. 11 (B)(a)-(c)).   Only one paramagnetic doublet attributed to

23     $Fe^{III}_2V^V_4O_{13}$ was observed for heat-treated 15ZCFV glass (Fig. 11(B)(d)).   These

24   results indicate that the crystallization behaviour is different in xZFV and yZCFV

25   glass samples.   Heat treatment of xZFV glass caused precipitation of $Fe_2V_4O_{13}$

26   phase, while that of 0ZCFV resulted in the precipitation of $FeVO_4$ as confirmed

27   from the corresponding XRD patterns.   The σ values of $Fe_2V_4O_{13}$ and $FeVO_4$

28   phases were respectively reported to be 10^{-2} S cm^{-1}[43] and $4.7 \cdot 10^{-5}$ S cm^{-1}[14].

29   Therefore, the precipitation of these crystalline phases doesn't significantly

30   contribute to the increase of electrical conductivity of xZFV and yZCFV after heat

31   treatment.   On the other hand, increases in T_g and T_c were confirmed from the

32   DTA measurements of analogous vanadate glasses of xNa$_2$O$\cdot$(90-x)V$_2$O$_5 \cdot 10P_2O_5$

33   and xNa$_2$O (89-x)V$_2$O$_5 \cdot 10P_2O_5 \cdot Fe_2O_3$[17].   Therefore, the thermal stability of

34   xZFV and yZCFV is increased by the introduction of Fe_2O_3.

1   Using equation (4) and by plotting and $(F(R_\mathrm{f})h\nu)^{1/n}$ as a function of photon

2   energy $h\nu$ (Tauc plot), optical bandgaps for indirect and direct transitions could be

3   estimated for before and after heat-treated 20ZFV and 0ZCFV glasses,

4   respectively.   It was seen that the best fitting occurs for $n = 1/2$, indicating a

5   direct allowed transition.   Due to the defective structure of glass amorphous, the

6   Tauc plot of 20ZFV and 0ZCFV glasses before and after heat treatment didn't

7   show clear baselines likely to be observed in the flat baseline of V_2O_5.   In order

8   to evaluate more precisely, the E_gs' of the studied samples are decided at the

9   tangential point of baseline and reflective line [44, 45].   Tauc plots of data from

10   samples 20ZFV and 0ZCFV before and after heat treatment are shown in Fig.12.

11   The E_g values of 4.02 and 3.88 eV were respectively estimated for 20ZFV and

12   0CZFV, while the smaller E_g s' of 2.30 and 2.27 eV were obtained for the

13   corresponding heat-treated samples. σ of 0ZCFV glass increased from 3.7×10^{-6}

14   to 6.7×10^{-1} S cm^{-1} after the heat treatment (See Fig. 4 (A)), which corresponds to

15   the decrease in E_g from 3.88 to 2.27 eV.   The E_g of V_2O_5 is estimated to be 2.35

16   eV, and the σ was reported to be $6.5\bullet10^{-6}$ S cm^{-1} [46, 47].   These results show

17   that the decrease in E_g due to heat-treatment of 0ZCFV glass causes an increase of

18   σ due to the precipitation of conductive β-vanadium bronze.   Although E_g

19   decreased from 4.02 to 2.30 eV, 20ZFV glass showed the smaller increase in

20   σ from 1.6×10^{-3} to 1.8×10^{-2} S cm^{-1} after heat treatment because the conductive

21   crystalline phase of $V_{0.03}Zr_{0.97}O_2$ is contained in the original sample (See Fig.

22   5(c)).   Similar decreases in bandgap energy were reported for heat-treated

23   $20BaO\bullet70V_2O_5\bullet Fe_2O_3$ glass partially substituted for metal oxides such as MnO_2,

24   Cu_2O and SnO_2[48].

25   In Fig. 13, the charge-discharge capacity of 20ZFV glass-ceramics and 0ZCFV

26   glass before and after the heat treatment are indicated.   Before the heat treatment,

27   discharge capacities of 118 mAh•g^{-1} in 20ZFV glass (Fig. 13 (A)-(a)) and 95 mAh

28   •g^{-1} in 0ZCFV(Fig. 13 (A)-(b)) were recorded after 5 cyclings, whereas the larger

29   discharge capacity of 153 mAh•g^{-1} in 20ZFV(Fig. 13 (B)-(b)) and 137 mAh•g^{-1} in

30   0ZCFV glass (Fig. 13 (B)-(b) were observed in heat-treated samples.   The larger

31   capacities observed in heat-treated 20ZFV and 0CZFV samples will be involved

32   with the higher electrical conductivity of 1.8×10^{-2} and 6.7×10^{-1} Scm^{-1},

33   respectively (See Figs. 3 and 4).   In Fig. 14, charge and discharge profiles are

34   plotted after 30 cyclings using 20ZVF and 0ZCFV glasses before and after the

1   heat treatment. The largest discharge capacities of 153 mAh g^{-1} were recorded

2   for 20ZFV after the heat treatment (Fig. 14(A) blue solid triangles). However,

3   after 30-time cycles, the capacity decreased to 69 mAh•g^{-1}. As for 0ZCFV glass

4   before the heat treatment, the smaller capacity of 89 mAh•g^{-1} was estimated after

5   5th cycling(Fig.14(B) red open triangles), which decreased to 56 mAh•g^{-1}

6   eventually. On the contrary, the heat-treated 0ZCFV glass showed a larger

7   capacity of 137 mAh•g^{-1}, ending up with 80 mAh•g^{-1} after 30 times cycling. In

8   our previous research, the discharge capacity of SIB containing

9     $25Na_2O•65V_2O_5•10P_2O_5$ glass before and after heat treatment at 450 ^{o}C for 100

10   min resulted in larger capacities of 184 and 173 mAh•g^{-1}, respectively [17].

11   Discharge capacities of 153 mAh•g^{-1} recorded for heat-treated 20ZFV glass

12   containing SIB showed comparable performance, although the test was carried out

13   under the larger current density of 50 mAg^{-1} (=2.0 mA cm^{-2}). Heat treatment of

14   20ZFV samples resulted in a slight increase of σ from 1.6×10^{-3} to 1.8×10^{-2} S cm^{-1}

15   due to the stable W_H 0.15 eV accompanying reduction of crystalline phase from

16    $V_{0.03}Zn_{0.97}O_2$ to $V_{0.05}Zr_{0.95}O_2$. On the other hand, 0ZCFV samples increased σ

17   from $3.7•10^{-6}$ to $6.7•10^{-1}$ S cm^{-1} due to a decrease in W_H 0.14 to 0.09 eV because of

18   the precipitation of β-$Ca_{0.17}V_2O_5$ caused by heat treatment. It is recognized that

19   a higher capacity of SIB was achieved by the heat-treated 20ZFV (= 153 mAh•g^{-1})

20   and that of 0CZFV (= 137 mAh•g^{-1}). In addition, T_g and T_c values of 20ZFV (T_g:

21   250 ^{o}C, T_c: 350 ^{o}C) and 0ZCFV (T_g: 284 ^{o}C, T_c: 387 ^{o}C) are higher than those of

22    $25Na_2O•65V_2O_5•10P_2O_5$ glass (T_g: 221 ^{o}C, T_c: 254 ^{o}C) [17]. Based on the

23   above-mentioned comparison, the reason for maintaining the high capacity of

24   20ZFV glass containing SIB is that 20ZFV glass before and after the heat-treated

25   samples have higher electrical conductivity and structural stability than those of

26   Na_2O-V_2O_5-P_2O_5 glass systems. In Table 3, a comparison of vanadates in terms

27   of cathode active performance in SIB is indicated. Unfortunately, previous

28   reports for cathode performances of calcia- and zirconia-vanadates are not

29   available. By comparing the SIB cathode active performance in this study with

30   other analogous sodium vanadates, the achieved capacities in this study by heat-

31   treated 20ZFV and 0ZCFV glasses of 153 and 137 mAh•g^{-1} are comparable or

32   larger than that previously reported sodium vanadium bronzes of $Na_{2.46}V_6O_{16}$ [51]

33   and $Na_{1.1}V_3O_{7.9}$ [52]. This may be due to the high electrical conductivity of heat-

34   treated 20ZFV and 0ZCFV. Based on the above results, we conclude that the

1   vanadate glass-ceramics containing Zr^{4+} or Ca^{2+} could be good candidates for the

2   cathode active material of SIB with high capacity and stability.

3

4. Summary

5   A relationship between the electrical conductivity, the cathode performance of

6   SIB, and the local structure of xZFV and yZCFV glass and glass-ceramics

7   prepared by heat treatment at 500 °C for 100 min were investigated.   Before

8   isothermal heat treatment, a gradual increase in electrical conductivity (σ) from

9   6.3×10^{-5} to 2.9×10^{-4}, 1.6×10^{-3} and 2.9×10^{-3} S cm^{-1} were observed in xZFV glass

10 with 'x' of 0, 10, 20 and 30, respectively.   After heat treatment at 500 °C for 100

11 min of 0ZCFV glass to form a glass-ceramics, a drastic increase in σ from 3.7×10^{-6}

12 to 6.7×10^{-1} S cm^{-1} was observed, whereas σ of sample 20ZFV showed a smaller

13 increase from 1.6×10^{-3} to 1.8×10^{-2} S cm^{-1}.   V-K edge XANES spectra of xZFV

14 glass showed little change in normalized pre-edge peak intensity as ZrO_2 content

15 was increased, indicating little change in either oxidation state and / or local

16 symmetry (coordination).   Moreover, after heat treatment, the normalized V-K

17 pre-edge peak intensity did not change between before and after heat treatment in

18 20ZFV samples.   By combining the results of XRD pattern and electrical

19 conductivity, β-vanadium bronzes precipitated in the heat-treated 0ZCFV played

20 an essential role in the drastic increase in σ.   The highest SIB performance with

21 the discharge capacity of 153 mAh•g^{-1} at the top was recorded for the heat-treated

22 20ZFV glass under the current density of 50 mA g^{-1}.   We can conclude that the

23 precipitation of stable vanadium bronzes in the studied system is important for

24 achieving the high capacity of SIB.

25

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