

**Development of Electrically Conductive ZrO<sub>2</sub>-CaO-Fe<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> 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<sub>2</sub>-CaO-**  
2 **Fe<sub>2</sub>O<sub>3</sub>-V<sub>2</sub>O<sub>5</sub> Glass and Glass-Ceramics as a New Cathode**  
3 **Active Material for Na-ion Batteries with High**  
4 **Performance**

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25 **Keywords** Na-ion battery, vanadate glass, electrical conductivity, <sup>57</sup>Fe-  
26 Mössbauer spectroscopy, XAFS

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1 **Abstract**

2 Glass-ceramics  $x\text{ZrO}_2 \cdot 10\text{Fe}_2\text{O}_3 \cdot (90-x)\text{V}_2\text{O}_5$  with ‘ $x$ ’ between 0 and 30 mol% and  
3  $y\text{ZrO}_2 \cdot (20-y)\text{CaO} \cdot 10\text{Fe}_2\text{O}_3 \cdot 70\text{V}_2\text{O}_5$  glass with ‘ $y$ ’ between 0 and 20 mol%,  
4 respectively abbreviated as  $x\text{ZFV}$  and  $y\text{ZCFV}$ , 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  $x\text{ZFV}$  and  $y\text{ZCFV}$  glass-ceramics were investigated by  $^{57}\text{Fe}$ -  
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  $x\text{ZFV}$  glass-ceramics  
11 showed the highest discharge capacity of  $153 \text{ mAh} \cdot \text{g}^{-1}$  under a current density of  
12  $50 \text{ mA} \cdot \text{g}^{-1}$ , which exhibited a high electrical conductivity of  $1.8 \times 10^{-2} \text{ Scm}^{-1}$ .  
13 Precipitation of  $\text{V}_{0.05}\text{Zr}_{0.95}\text{O}_2$  and  $\text{Fe}_2\text{V}_4\text{O}_{13}$  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  $\text{V}^{\text{V}}$  to  $\text{V}^{\text{IV}}$ . 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,  $^{57}\text{Fe}$ -Mössbauer spectroscopy, XAFS

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# 1 **1. Introduction**

2       Lithium-ion batteries (LIB) are widely utilized as a secondary battery for  
3 electrical facilities such as laptop PCs and smartphones because of the high  
4 theoretical capacity of 3861 mAh g<sup>-1</sup>[1]. However, the small abundance of Li in  
5 the Earth's crust (0.006) will cause future scarcity and an increase in the price of  
6 LIB [1]. Therefore, post-lithium-ion batteries with the large capacity and long  
7 lifetime have been keenly investigated. Among these, sodium-ion batteries (SIB)  
8 are strong candidates for post-lithium-ion batteries because of the high availability  
9 of sodium, having a larger abundance in the Earth's crust of 2.63 and a high  
10 theoretical capacity of 1166 mAh•g<sup>-1</sup> next to LIB [1-3]. Many researchers have  
11 investigated SIB with high performances. For example, Yasin *et al.* successfully  
12 prepared SIB with the capacity of 122 mAh•g<sup>-1</sup> maintained after 4000 cycles by  
13 using graphene as the anode [4], which leads to an oxygen reduction catalyst [5].  
14 Concerning the development of new cathode active materials for SIB,  
15 30Na<sub>2</sub>O•40FeO•30P<sub>2</sub>O<sub>5</sub> glass exhibited an initial discharge capacity of 115 mAh  
16 •g<sup>-1</sup> when it was incorporated as a cathode active material of SIB[6]. In addition,  
17 NASICON-type Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> nanoparticles prepared by an electrospinning  
18 method as a cathode of SIB showed a larger initial discharge capacity of 94 mAh  
19 •g<sup>-1</sup> than that of the bulk material of 56 mAh•g<sup>-1</sup> [7]. Furthermore, Uchaker *et al.*  
20 reported that amorphous V<sub>2</sub>O<sub>5</sub> prepared by a combination of sol-gel method and  
21 electrochemical deposition showed a capacity of 241 mAh•g<sup>-1</sup> [8]. These  
22 previous studies indicate that amorphous vanadates present high potentially novel  
23 opportunities for utilizing a new cathode active material for SIB.

24       Vanadate glasses and glass-ceramics are known semiconductors, with  
25 electrical conductivities ( $\sigma$ ) of 10<sup>-7</sup>-10<sup>-5</sup> S cm<sup>-1</sup>, attributed to 3d electron (polaron)  
26 hopping from V<sup>VI</sup> or V<sup>III</sup> to V<sup>V</sup> [9, 10]. It has been reported that a drastic  
27 increase in the electrical conductivity ( $\sigma$ ) from 10<sup>-7</sup> to 10<sup>0</sup> S cm<sup>-1</sup> took place in  
28 semiconducting barium iron vanadate glass, *e.g.*, 20BaO•10Fe<sub>2</sub>O<sub>3</sub>•70V<sub>2</sub>O<sub>5</sub> glass,  
29 when it was heat-treated at temperatures higher than glass transition temperature  
30 ( $T_g$ ) or crystallization temperature ( $T_c$ ) [11, 12], thus forming a glass-ceramic.  
31 Furthermore, Kubuki reported that the  $\sigma$  value of alkaline iron vanadate glass  
32 (R<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub>-Fe<sub>2</sub>O<sub>3</sub>, R: Li, Na) was sensitively affected by the crystalline phase  
33 precipitated in the glass system [13]. For example, 20Na<sub>2</sub>O•70V<sub>2</sub>O<sub>5</sub>•10Fe<sub>2</sub>O<sub>3</sub>  
34 glasses showed the largest  $\sigma$  of 2.5×10<sup>-2</sup> S cm<sup>-1</sup> after heat treatment at 500 °C for

1 100 min, but a decrease in  $\sigma$  was observed when heat-treated at 550 °C for 100  
2 min due to the precipitation of  $\text{FeVO}_4$  having the smaller  $\sigma$  of  $4.7 \times 10^{-5} \text{ S cm}^{-1}$   
3 [14]. These results show that  $\sigma$  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  $15\text{Li}_2\text{O} \cdot 10\text{Fe}_2\text{O}_3 \cdot 20\text{SnO}_2 \cdot 5\text{P}_2\text{O}_5 \cdot 50\text{V}_2\text{O}_5$  glass resulted  
8 in a remarkable increase in  $\sigma$  amounting to the order of  $10^{-2} \text{ S cm}^{-1}$  and a large  
9 capacity of  $493 \text{ mAh} \cdot \text{g}^{-1}$  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  $x\text{Na}_2\text{O} \cdot (90-x)\text{V}_2\text{O}_5 \cdot 10\text{P}_2\text{O}_5$  glass with  
13 ‘ $x$ ’ of 5, 25 and 45 mol%, provided a relatively high discharge capacity of 150–  
14 200  $\text{mAh} \cdot \text{g}^{-1}$  after recycling of 5 times under the voltage between 0.8 and 3.6 V  
15 with the current density of  $0.2 \text{ mA cm}^{-2}$  [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  $x\text{NPV}$  glass,  
19 increase of stability is expected when  $\text{Na}^+$  is substituted for other cations with  
20 high valence states such as  $\text{Ca}^{2+}$  and  $\text{Zr}^{4+}$  because  $\text{CaO-ZrO}_2$  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  $\text{ZrO}_2\text{-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$  and  $\text{CaO-}$   
26  $\text{ZrO}_2\text{-V}_2\text{O}_5\text{-Fe}_2\text{O}_3$  were investigated by  $^{57}\text{Fe}$ -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  $x\text{ZrO}_2 \cdot 10\text{Fe}_2\text{O}_3 \cdot (90-x)\text{V}_2\text{O}_5$  ( $x=0-30$  in mol %) and  $y\text{ZrO}_2 \cdot (20-$

1  $y$ )CaO•10Fe<sub>2</sub>O<sub>3</sub>•70V<sub>2</sub>O<sub>5</sub> glasses ( $y=0-20$  in mol%), respectively abbreviated as  
 2  $x$ ZFV and  $y$ ZCFV, were prepared by a conventional melt-quenching method.  
 3 Weighed amounts of reagent-grade ZrO<sub>2</sub> (Wako:264-00485), CaCO<sub>3</sub> (Wako:030-  
 4 00385), Fe<sub>2</sub>O<sub>3</sub> (Wako:096-04825) and V<sub>2</sub>O<sub>5</sub> (Wako:225-00125) were well mixed  
 5 in an agate mortar, and the mixture in a platinum crucible was melted at 1200 °C  
 6 for 1 h in an electric muffle furnace. Homogeneous black samples of  $x$ ZFV and  
 7  $y$ ZCFV 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 °C for  
 9 100 min in air. For <sup>57</sup>Fe-Mössbauer measurement, an enriched isotope of  
 10 <sup>57</sup>Fe<sub>2</sub>O<sub>3</sub> (95.54%) was used for the sample preparation.

11 Measurements of differential thermal analysis (DTA) were performed from  
 12 room temperature (RT) to 700 °C under the heating rate ( $\alpha$ ) of 10 K•min<sup>-1</sup> using  
 13 Themo plus TG8120 (Rigaku). Ten milligrams of well-pulverized samples and a  
 14 reference of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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

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

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 °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  $\sigma$  ( $\Omega^{-1}\cdot\text{cm}^{-1}$ ) was estimated using the following equation, *i.e.*,

29

$$30 \quad \sigma = R_s^{-1} \cdot S^{-1} \cdot l \quad (2),$$

31

32 where  $R_s$ ,  $S$  and  $l$  are electrical resistivity (in  $\Omega$ ) obtained from a slope of a  
 33 straight line of  $E$  vs.  $I$  plot, surface area (in cm<sup>2</sup>) and the distance between the

1 electrodes (in cm), respectively. For conductivity measurements, each glass  
2 block sample was ground into a rectangular plate of which edges were coated with  
3 Ag solder to attach lead lines. By using a RINT-TTR III (Rigaku) X-ray  
4 diffractometer, XRD patterns were recorded using Cu-K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ )  
5 between  $2\theta$  of  $10^\circ$  and  $80^\circ$  with data interval and scanning rate of  $0.02^\circ$  and  $5^\circ$   
6  $\text{min}^{-1}$ , respectively. The obtained XRD patterns were analyzed by PDXL2  
7 (Rigaku) software with the database of ICDD PDF4 (Light Stone). Surface  
8 observation of the prepared samples using scanning electron microscopy (SEM)  
9 was performed by VE-9800 (Keyence) under the applied voltage of 2 kV with a  
10 magnitude of  $5 \times 10^3$ . X-ray absorption spectra at the vanadium *K*-edge using  
11 synchrotron radiation were measured at room temperature at beamline BL11 of  
12 the Saga Light Source (Yayoigaoka 8-7, Tosu, Saga 841-0005, JAPAN) using a  
13 double Si (111) monochromator. The thickness of the samples was controlled to  
14 enable transmission mode measurement (V *K*-edge).  $^{57}\text{Fe}$ -Mössbauer spectra  
15 were recorded at room temperature by a constant acceleration method. The  
16 system was composed of a driving unit (MDU-1200, Wissel), a digital function  
17 generator (DFG-1000, Wissel), a proportion counter (4546, Niki Kogei), a  
18 preamplifier (142IH, ORTEC), a high voltage supply (456, ORTEC), an amplifier  
19 (485, ORTEC) and a multichannel analyzer (EASY-MCS, ORTEC). A  $^{57}\text{Co}$   
20 (Rh) source with the radioactivity of 925 MBq (MCo7. 123, produced on Jan. 10,  
21 2018, by Ritverc) and  $\alpha$ -Fe foil were used as a source and a reference of isomer  
22 shift ( $\delta$ ), respectively. Obtained spectra were analyzed by Mosswin4.0 with  
23 Lorentzian fitting. The optical bandgap was estimated from diffuse reflectance  
24 UV-Vis spectroscopy recorded on Shimadzu UV-3600 spectrometer with an  
25 integrating sphere attachment (ISR-3100, Shimadzu). Estimation of optical band  
26 gap was carried out by diffuse reflectance UV-Vis spectroscopy and using the  
27 Kubelka–Munk equation [19]:

28

$$29 \quad F(R_f) = (1-R_f)^2 \cdot (2R_f)^{-1} \quad (3),$$

30

31 where  $R_f$  is the reflectance. Further information was obtained by the Tauc plots  
32 [20]:

33

$$\alpha \cdot h \cdot \nu = A \cdot (h \nu - E_g)^n \quad (4),$$

where  $A$  is the proportionality constant,  $\alpha$  is the absorption coefficient (here,  $F(R)$  being directly proportional to  $\alpha$ ),  $\nu$  is the frequency of light and  $E_g$  is the bandgap. The value of  $n$  is dependent on the nature of the transition:  $n$  is 1/2 for a directly allowed transition and 2 for an indirectly allowed transition [21, 22]. Sodium-ion battery (SIBs) were prepared in 2032 type containing the anode of metallic Na (Kishida: 620-70852), the electrolyte of NaClO<sub>4</sub> / propylene carbonate solution (Tomypure: LIPASTE-P/S1), and the cathode with the ratio of sample: acetylene black (AB, Strem chemicals: 06-0025): polytetrafluoroethylene (PTFE, Wako: 165-13412) of 70:25:5. The cathode and anode were respectively loaded by 30 and 90 mg, where each electrode had a 1cm diameter. An ECD8-0.5-LUs1 (Matsusada Precision) measured the charge-discharge capacity performance by repeating 30 times under the voltage window of 0.8-3.6V, a current density of 50 mA g<sup>-1</sup> (=2.0 mA cm<sup>-2</sup>), and the cut-off current of 0.5 mA in the charging process under CCCV mode.

### 3. Results and Discussion

DTA curves of  $x$ ZFV and  $y$ ZCFV samples are depicted in Figure 2. In the case of  $x$ ZFV glass,  $T_g$  and  $T_c$  respectively varied from 244 $\pm$ 5 to 250 $\pm$ 5, 250 $\pm$ 5, and 251 $\pm$ 5 °C, and from 324 $\pm$ 2 to 360 $\pm$ 2, 350 $\pm$ 2 and 361 $\pm$ 2 °C with ZrO<sub>2</sub> concentration ( $x$ ). On the other hand, a decrease in  $T_g$  from 284 to 250 °C and  $T_c$  from 387 to 350 °C were observed for  $y$ ZCFV with ZrO<sub>2</sub> concentration ( $y$ ). Decreases in  $T_g$  and  $T_c$  observed for  $y$ ZCFV imply that thermal durability was decreased when Zr<sup>4+</sup> was replaced by Ca<sup>2+</sup> because the network forming cation of vanadium is partially reduced from V<sup>5+</sup> to V<sup>4+</sup>. On the contrary, the role of Zr<sup>4+</sup> in the glass network of  $x$ ZFV is not clear due to the high oxidation number of 4+. Based on the  $T_g$ 's and  $T_c$ 's of  $x$ ZFV and  $y$ ZCFV glasses, the isothermal annealing was conducted at 500 °C for 100 min. From the Kissinger plot,  $E_a$ 's were calculated 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  $x$ ZFV glass with ' $x$ ' of 0, 10, 20 and 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  $y$ ZCFV glass with  $y$  of 0, 5, 10, 15 and 20. Because chemical bond energies were reported to be 2.6 eV for



1 Fe<sup>III</sup>-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 ( $\sigma$ ) and activation energy of electrical  
4 conduction ( $W_H$ ) of  $x$ ZFV glass were plotted against ZrO<sub>2</sub> content before and after  
5 heat treatment at 500 °C for 100 min. Before the heat treatment, a gradual  
6 increase in  $\sigma$  was observed from  $6.3 \times 10^{-5}$  to  $2.9 \times 10^{-4}$ ,  $1.6 \times 10^{-3}$  and  $2.9 \times 10^{-3}$  S cm<sup>-1</sup>  
7 with an increase of ZrO<sub>2</sub> content in  $x$ ZFV 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

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

12

13 where  $T$ ,  $\sigma_0$  and  $k$  are measurement temperature (in K), conductivity at a given  
14 temperature, and Boltzmann constant ( $1.380 \times 10^{-23}$  JK<sup>-1</sup>). 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  $0.18_{\pm 0.01}$  ( $x=0$ ) to  $0.16_{\pm 0.02}$  ( $x=10$ ),  $0.15_{\pm 0.02}$   
18 ( $x=20$ ) and  $0.13_{\pm 0.01}$  ( $x=30$ ) eV, and from  $0.16_{\pm 0.02}$  ( $x=0$ ) to  $0.15_{\pm 0.02}$  ( $x=10$ ),  
19  $0.15_{\pm 0.02}$  ( $x=20$ ) and  $0.14_{\pm 0.02}$  ( $x=30$ ) were observed before and after heat treatment,  
20 respectively. These results indicate that the probability of electron hopping was  
21 increased by substituting ZrO<sub>2</sub> for V<sub>2</sub>O<sub>5</sub> in  $x$ ZFV glass, regardless of the heat  
22 treatment. It is considered that the increase of  $\sigma$  in  $x$ ZFV glass before and after  
23 the heat treatment is caused by the reduction of vanadium with ZrO<sub>2</sub> content. In  
24 Fig. 4,  $\sigma$  and  $W_H$  of  $y$ ZCFV glass were plotted against ZrO<sub>2</sub> content before and  
25 after heat treatment at 500 °C for 100 min. As shown in open circles in Fig. 4  
26 (A),  $\sigma$  of  $y$ ZCFV glass before the heat treatment was increased from  $3.7 \times 10^{-6}$  to  
27  $1.6 \times 10^{-3}$  S cm<sup>-1</sup> with ZrO<sub>2</sub> content because of the reduction of vanadium ion from  
28 V<sup>V</sup> to V<sup>IV</sup>. As for heat-treated  $y$ ZCFV glass,  $\sigma$  decreased from  $6.7 \times 10^{-1}$  to  
29  $1.8 \times 10^{-2}$  S cm<sup>-1</sup>, while  $W_H$  increased from 0.09 to 0.15 eV with ZrO<sub>2</sub>  
30 concentration. It is noted that  $\sigma$  dramatically increased from  $3.7 \times 10^{-6}$  to  $6.7 \times 10^{-1}$   
31 S cm<sup>-1</sup> when 0ZCFV glass was heat-treated at 500 °C for 100 min, while  
32 differences in  $\sigma$  between before and after heat treatment become smaller in the  
33 case of  $y$ ZCFV with 'y' of larger than 5 mol%.

1 XRD patterns of  $x$ ZFV glass with ‘ $x$ ’ of 0, 10, 20 and 30 recorded before the  
 2 heat treatment are shown in Fig. 5. A halo pattern was observed for  $x$ ZFV glass  
 3 with ‘ $x$ ’ of 0 and 10, indicating the presence of an amorphous structure in the  
 4 glass matrix as shown in Fig. 5 (a)-(b). On the other hand, a halo pattern  
 5 superimposed by intense sharp peaks attributed to crystalline phases of  
 6  $V_{0.03}Zr_{0.97}O_2$  (PDF No. 01-072-6680, open circles) and weak sharp peaks  
 7 attributed to crystalline  $V_2O_5$  (PDF No. 01-089-2482, solid circles) and  $VO_2$  (PDF  
 8 No. 03-065-7960, solid rhombuses) were also observed for samples 20ZFV and  
 9 30ZFV (see Fig. 5 (c)-(d)). The crystalline phase of  $V_{0.03}Zr_{0.97}O_2$  was  
 10 unexpectedly produced because a clear surface was observed for as-quenched  
 11 20ZFV glass. Peaks attributed to  $V_2O_5$  were disappeared with increasing ‘ $x$ ’  
 12 from 20 to 30, while those due to  $VO_2$  appeared, suggesting that  $V^V$  was partially  
 13 reduced into  $V^{IV}$  with increasing  $ZrO_2$  content in  $x$ ZFV glass.  $V_xZr_{1-x}O_2$  called  
 14 “vanadium-zirconia yellow baddeleyite”, is a well-known ceramic pigment. The  
 15 oxidation number 4+ in vanadium was found in both solid solutions (monoclinic  
 16 and tetragonal) based on zirconia crystalline forms [25-27]. Hence, the presence  
 17 of the crystalline phase of  $V_xZr_{1-x}O_2$  ( $0 \leq x \leq 0.1$ ) could be evidential to conclude  
 18 that  $V_2O_5$  was reduced to  $VO_2$  during sample preparation. XRD patterns for  
 19 20ZFV and 0ZCFV glass samples before and after the heat treatment are  
 20 illustrated in Fig. 6. The XRD pattern for sample 20ZFV before the heat-  
 21 treatment was mentioned in the previous section, while crystalline phases of  
 22  $V_{0.05}Zr_{0.95}O_2$  (PDF No. 01-072-6681: double circles) and  $Fe_2V_4O_{13}$  (PDF No. 01-  
 23 089-5460: solid triangles) were detected in the heat-treated sample. Precipitation  
 24 of  $V_{0.05}Zr_{0.95}O_2$  phase observed for heat-treated 20ZFV shows that the fraction of  
 25  $V^{IV}$  is increased. The XRD pattern for sample 0ZCFV showed a halo pattern  
 26 characteristic of glass amorphous structure, whereas some sharp intense peaks  
 27 attributed to  $Ca_{0.17}V_2O_5$  (PDF No. 00-026-1165: open triangles),  $CaV_2O_6$  (PDF  
 28 No. 01-073-0186: open squares),  $FeVO_4$  (PDF No. 00-038-1372: open  
 29 rhombuses) and  $V_2O_5$  were observed for the heat-treated samples (see Fig. 6(B)  
 30 (a)-(b)). The crystalline phase  $Ca_{0.17}V_2O_5$  is called beta-vanadium bronze ( $\beta$ -  
 31  $M_xV_2O_5$ ), a highly conductive anisotropic semiconductor with  $\sigma$  of  $10^0$ - $10^1$  S  $cm^{-1}$   
 32 at room temperature due to small polaron hopping [28-33]. It was reported that  
 33 highly conductive glass-ceramics containing vanadium bronze could be produced  
 34 through the crystallization of vanadate glasses. Hirashima *et al.* reported that the

1 DC conductivity of the crystallized  $\text{Na}_2\text{O-V}_2\text{O}_5\text{-P}_2\text{O}_5$  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  $\sigma$  values  
5 between 20ZFV and 0CZVF glasses, the network modifier ( $\text{Ca}^{2+}$ , in this study)  
6 seems to have played a significant role in forming the vanadium bronze ( $\text{M}_x\text{V}_2\text{O}_5$ )  
7 phase.

8 In Figure 7, SEM images of 20ZFV and 0CZVF are indicated. We could  
9 confirm a crystalline of  $\text{Zr}_{0.03}\text{V}_{0.97}\text{O}_2$  with the particle size of about 50  $\mu\text{m}$  in  
10 20ZFV before treatment (Fig. 7 (A-a)), while rod-like crystalline of  $\text{Zr}_{0.05}\text{V}_{0.95}\text{O}_2$   
11 and  $\text{Fe}_2\text{V}_4\text{O}_{13}$  with the length of 20  $\mu\text{m}$  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  $\mu\text{m}$  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 *x*ZFV and *y*ZCFV glasses.  
17 Fig. 8 (A) shows the normalized V *K*-edge spectra of *x*ZFV glass measured before  
18 heat treatment, together with spectra for  $\text{V}_2\text{O}_5$ ,  $\text{VO}_2$  and  $\text{V}_2\text{O}_3$  chemical reagents.  
19 The V *K* pre-edge peaks for *x*ZFV 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  $\text{V}_2\text{O}_5$ ,  $\text{VO}_2$ , and  $\text{V}_2\text{O}_3$  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  $1s\text{-}3d$  electronic  
25 transition [35]. The intensity of the V *K*-pre-edge peak exhibited little change  
26 with increasing  $\text{ZrO}_2$  content, except for a small decrease in intensity with the  
27 highest  $\text{ZrO}_2$  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- $\text{O}_x$  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  $x$ ZFV 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  $20$ ZFV and  $0$ ZCFV 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  $0$ ZCFV 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  $20$ ZFV. 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  $\text{VO}_2$ , *i.e.* confirming  
18 the presence of  $\text{V}^{4+}$ . Indeed, the normalized V- $K$  pre-edge peak intensity did not  
19 change between before and after the heat-treatment of  $x$ ZFV glass, although that  
20 of  $0$ ZCFV 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  $x$ ZFV glasses measured before  
26 and after heat treatment at  $500$  °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  $\delta$  of  $0.39_{\pm 0.01}$  mm s<sup>-1</sup> and closely similar  
30 quadrupole splitting ( $\Delta$ ) from  $0.67$  to  $0.68, 0.74$  and  $0.72_{\pm 0.02}$  mm s<sup>-1</sup> were obtained  
31 by fitting spectra, with an increasing  $\text{ZrO}_2$  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  $\text{Fe}^{\text{III}}\text{O}_4$  tetrahedra [39] was slightly increased as a result of the substitution of  $\text{ZrO}_2$   
34 for  $\text{V}_2\text{O}_5$ , as previously observed in  $20\text{BaO}\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{WO}_3\cdot (70-x)\text{V}_2\text{O}_5$  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 ( $\delta$ ) and quadrupole splitting ( $\Delta$ ) 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 °C for 100 min are shown in Fig. 11  
 8 and Table 2. Before the heat treatment, an identical  $\delta$  of  $0.38_{\pm 0.01}$   $mm\ s^{-1}$  and  
 9 almost identical  $\Delta$  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,  $\Delta$  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  $Fe^{III}V^V O_4$  [13, 42] with  $\delta$  and  $\Delta$  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  $\sigma$  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  $xNa_2O \cdot (90-x)V_2O_5 \cdot 10P_2O_5$   
 33 and  $xNa_2O \cdot (89-x)V_2O_5 \cdot 10P_2O_5 \cdot Fe_2O_3$ [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  $(F(R_f)h\nu)^{1/n}$  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  $E_g$ 's 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 0ZCFV, while the smaller  $E_g$ 's of 2.30 and 2.27 eV were obtained for the  
 13 corresponding heat-treated samples.  $\sigma$  of 0ZCFV glass increased from  $3.7 \times 10^{-6}$   
 14 to  $6.7 \times 10^{-1} \text{ S cm}^{-1}$  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  $\sigma$  was reported to be  $6.5 \cdot 10^{-6} \text{ S cm}^{-1}$  [46, 47]. These results show  
 17 that the decrease in  $E_g$  due to heat-treatment of 0ZCFV glass causes an increase of  
 18  $\sigma$  due to the precipitation of conductive  $\beta$ -vanadium bronze. Although  $E_g$   
 19 decreased from 4.02 to 2.30 eV, 20ZfV glass showed the smaller increase in  
 20  $\sigma$  from  $1.6 \times 10^{-3}$  to  $1.8 \times 10^{-2} \text{ S cm}^{-1}$  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  $20\text{BaO} \cdot 70\text{V}_2\text{O}_5 \cdot \text{Fe}_2\text{O}_3$  glass partially substituted for metal oxides such as  $\text{MnO}_2$ ,  
 24  $\text{Cu}_2\text{O}$  and  $\text{SnO}_2$ [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  $118 \text{ mAh} \cdot \text{g}^{-1}$  in 20ZfV glass (Fig. 13 (A)-(a)) and  $95 \text{ mAh}$   
 28  $\cdot \text{g}^{-1}$  in 0ZCFV (Fig. 13 (A)-(b)) were recorded after 5 cyclings, whereas the larger  
 29 discharge capacity of  $153 \text{ mAh} \cdot \text{g}^{-1}$  in 20ZfV (Fig. 13 (B)-(b)) and  $137 \text{ mAh} \cdot \text{g}^{-1}$  in  
 30 0ZCFV glass (Fig. 13 (B)-(b)) were observed in heat-treated samples. The larger  
 31 capacities observed in heat-treated 20ZfV and 0ZCFV samples will be involved  
 32 with the higher electrical conductivity of  $1.8 \times 10^{-2}$  and  $6.7 \times 10^{-1} \text{ Scm}^{-1}$ ,  
 33 respectively (See Figs. 3 and 4). In Fig. 14, charge and discharge profiles are  
 34 plotted after 30 cyclings using 20ZfV and 0ZCFV glasses before and after the

1 heat treatment. The largest discharge capacities of  $153 \text{ mAh g}^{-1}$  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  $69 \text{ mAh}\cdot\text{g}^{-1}$ . As for 0ZCFV glass  
 4 before the heat treatment, the smaller capacity of  $89 \text{ mAh}\cdot\text{g}^{-1}$  was estimated after  
 5 5th cycling (Fig.14(B) red open triangles), which decreased to  $56 \text{ mAh}\cdot\text{g}^{-1}$   
 6 eventually. On the contrary, the heat-treated 0ZCFV glass showed a larger  
 7 capacity of  $137 \text{ mAh}\cdot\text{g}^{-1}$ , ending up with  $80 \text{ mAh}\cdot\text{g}^{-1}$  after 30 times cycling. In  
 8 our previous research, the discharge capacity of SIB containing  
 9  $25\text{Na}_2\text{O}\cdot 65\text{V}_2\text{O}_5\cdot 10\text{P}_2\text{O}_5$  glass before and after heat treatment at  $450 \text{ }^\circ\text{C}$  for 100  
 10 min resulted in larger capacities of 184 and  $173 \text{ mAh}\cdot\text{g}^{-1}$ , respectively [17].  
 11 Discharge capacities of  $153 \text{ mAh}\cdot\text{g}^{-1}$  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  $50 \text{ mA g}^{-1}$  ( $=2.0 \text{ mA cm}^{-2}$ ). Heat treatment of  
 14 20ZFV samples resulted in a slight increase of  $\sigma$  from  $1.6\times 10^{-3}$  to  $1.8\times 10^{-2} \text{ S cm}^{-1}$   
 15 due to the stable  $W_{\text{H}} 0.15 \text{ eV}$  accompanying reduction of crystalline phase from  
 16  $\text{V}_{0.03}\text{Zn}_{0.97}\text{O}_2$  to  $\text{V}_{0.05}\text{Zr}_{0.95}\text{O}_2$ . On the other hand, 0ZCFV samples increased  $\sigma$   
 17 from  $3.7\cdot 10^{-6}$  to  $6.7\cdot 10^{-1} \text{ S cm}^{-1}$  due to a decrease in  $W_{\text{H}} 0.14$  to  $0.09 \text{ eV}$  because of  
 18 the precipitation of  $\beta\text{-Ca}_{0.17}\text{V}_2\text{O}_5$  caused by heat treatment. It is recognized that  
 19 a higher capacity of SIB was achieved by the heat-treated 20ZFV ( $= 153 \text{ mAh}\cdot\text{g}^{-1}$ )  
 20 and that of 0CZVF ( $= 137 \text{ mAh}\cdot\text{g}^{-1}$ ). In addition,  $T_{\text{g}}$  and  $T_{\text{c}}$  values of 20ZFV ( $T_{\text{g}}$ :  
 21  $250 \text{ }^\circ\text{C}$ ,  $T_{\text{c}}$ :  $350 \text{ }^\circ\text{C}$ ) and 0ZCFV ( $T_{\text{g}}$ :  $284 \text{ }^\circ\text{C}$ ,  $T_{\text{c}}$ :  $387 \text{ }^\circ\text{C}$ ) are higher than those of  
 22  $25\text{Na}_2\text{O}\cdot 65\text{V}_2\text{O}_5\cdot 10\text{P}_2\text{O}_5$  glass ( $T_{\text{g}}$ :  $221 \text{ }^\circ\text{C}$ ,  $T_{\text{c}}$ :  $254 \text{ }^\circ\text{C}$ ) [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  $\text{Na}_2\text{O-V}_2\text{O}_5\text{-P}_2\text{O}_5$  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  $137 \text{ mAh}\cdot\text{g}^{-1}$  are comparable or  
 32 larger than that previously reported sodium vanadium bronzes of  $\text{Na}_{2.46}\text{V}_6\text{O}_{16}$  [51]  
 33 and  $\text{Na}_{1.1}\text{V}_3\text{O}_{7.9}$  [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.

#### 4 **4. Summary**

5 A relationship between the electrical conductivity, the cathode performance of  
6 SIB, and the local structure of  $xZrFV$  and  $yZrCFV$  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 ( $\sigma$ ) from  
9  $6.3 \times 10^{-5}$  to  $2.9 \times 10^{-4}$ ,  $1.6 \times 10^{-3}$  and  $2.9 \times 10^{-3}$  S  $cm^{-1}$  were observed in  $xZrFV$  glass  
10 with 'x' of 0, 10, 20 and 30, respectively. After heat treatment at 500 °C for 100  
11 min of  $0ZrCFV$  glass to form a glass-ceramics, a drastic increase in  $\sigma$  from  $3.7 \times 10^{-6}$   
12 to  $6.7 \times 10^{-1}$  S  $cm^{-1}$  was observed, whereas  $\sigma$  of sample  $20ZrFV$  showed a smaller  
13 increase from  $1.6 \times 10^{-3}$  to  $1.8 \times 10^{-2}$  S  $cm^{-1}$ . V-K edge XANES spectra of  $xZrFV$   
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  $20ZrFV$  samples. By combining the results of XRD pattern and electrical  
19 conductivity,  $\beta$ -vanadium bronzes precipitated in the heat-treated  $0ZrCFV$  played  
20 an essential role in the drastic increase in  $\sigma$ . The highest SIB performance with  
21 the discharge capacity of  $153 \text{ mAh} \cdot \text{g}^{-1}$  at the top was recorded for the heat-treated  
22  $20ZrFV$  glass under the current density of  $50 \text{ mA g}^{-1}$ . 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.

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