

# Enhancement of Electrical Conductivity and Thermal Stability of Iron- or Tin-substituted Vanadate Glass and Glass-Ceramics nanocomposite to be used as a High-Performance Cathode Active Material in Sodium-Ion Batteries

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## 1 Introduction

Rechargeable Li-ion batteries (LIBs) are now commonly applied as a portable energy source for powering various electronic devices and household appliances. Meanwhile, there is still more interest in achieving high-capacity rechargeable batteries for broader applications like electric vehicles (EVs) while maintaining their safety and economic feasibility [1]. Although having high performance with a theoretical capacity of 274 mAh g<sup>-1</sup> for LiCoO<sub>2</sub> cathode [2], commercially available Li-ion battery faces the crisis of Li and Co scarcities in the future because of their abundance in Earth's crust is only about 20 and 25 ppm respectively [3]. Due to this reason, new secondary batteries composed of ubiquitous elements with high capacity and recyclability are intensively investigated. Many scientists have recently started looking for new elements abundant in nature and inexpensive to utilize in batteries. Many batteries have recently been developed that apply different chemical elements instead of lithium, such as Al<sup>3+</sup> [4], Ca<sup>2+</sup> [5], K<sup>+</sup> [6], Mg<sup>2+</sup> [7] and Na<sup>+</sup> [8]. The Na-ion battery with a theoretical capacity of 235 mAh g<sup>-1</sup> for NaCoO<sub>2</sub> cathode [2] is one of the most promising candidates for a post-Li-ion battery age because Na has an abundance in Earth's crust of 23600 ppm, which is much larger than that of Li and Co [3]. As a result, the interest in Na-ion batteries (SIBs) as a viable alternative to LIBs for large-scale energy storage has grown significantly since 2010 [9].

To develop a Na-ion battery with high capacity, vanadate glass and ceramics are suitable candidates for the cathode active material because the expected theoretical capacity is about 400 mAh g<sup>-1</sup> [10]. It was reported that vanadate bronze (M<sub>x</sub>V<sub>2</sub>O<sub>5</sub>, M: Na<sup>+</sup>, Ag<sup>+</sup>) showed relatively high cathode performance when applied in a Na-ion battery [11]. For example, the capacity of 62 and 83 mAh g<sup>-1</sup> was recorded for Na<sub>2.46</sub>V<sub>6</sub>O<sub>16</sub> and Na<sub>0.33</sub>V<sub>2</sub>O<sub>5</sub> under the current density of 1.5 and 0.02 mA g<sup>-1</sup>, respectively [11]. Also, vanadate glass upper is a promising cathode material for Na-ion batteries because of the large pore size due to the amorphous structure and the electrical conductivity ( $\sigma$ ) of about 10<sup>-7</sup>~10<sup>-5</sup> S cm<sup>-1</sup>. This latter is due to electron hopping between the vanadium ions of different oxidation states [12]. In our previous study, a large initial discharge capacity of 382.3 mAh g<sup>-1</sup> was recorded for a Li-ion battery which contained 15LiO<sub>2</sub>•10Fe<sub>2</sub>O<sub>3</sub>•20SnO<sub>2</sub>•5P<sub>2</sub>O<sub>5</sub>•70V<sub>2</sub>O<sub>5</sub> glass cathode with the electrical conductivity ( $\sigma$ ) of 7.4•10<sup>-7</sup>

S cm<sup>-1</sup> [13, 14]. The <sup>57</sup>Fe- and <sup>119</sup>Sn- Mössbauer spectra of this glass showed that Fe<sup>III</sup> was substituted at the network forming site of vanadium ions with the isomer shift ( $\delta$ ) of 0.35 mm s<sup>-1</sup> and quadrupole splitting ( $\Delta$ ) of 0.88 mm s<sup>-1</sup>. In comparison, Sn<sup>IV</sup> accommodated network modifying sites of Li-ions showing  $\delta$  of 0.08 mm s<sup>-1</sup> and  $\Delta$  of 0.52 mm s<sup>-1</sup> [15]. Recently, Kubuki *et al.* found that Na-ion battery with a cathode of xNa<sub>2</sub>O•(90-x)V<sub>2</sub>O<sub>5</sub>•10P<sub>2</sub>O<sub>5</sub> glass with 'x' of 5, 25 and 45 mol% showed a large initial capacity of 307, 184 and 258 mAh g<sup>-1</sup>, respectively, and a small irreversible capacity of 86, 6 and 21 mAh g<sup>-1</sup> under the current density of 5 mA g<sup>-1</sup> [16]. These results imply that vanadate glass can be a better cathode active material for Na-ion batteries if Fe<sub>2</sub>O<sub>3</sub> or SnO<sub>2</sub> is introduced.

In this work, a novel vanadium glass and glass-ceramics nanocomposite series have been prepared. The relationships between local structure, physical properties and cathode-active properties in the Na-ion battery of Fe<sub>2</sub>O<sub>3</sub> or SnO<sub>2</sub> substituted Na<sub>2</sub>O-V<sub>2</sub>O<sub>5</sub>-P<sub>2</sub>O<sub>5</sub> glass were investigated to develop a Na-ion battery with a high capacity and recyclability.

## 2 Experiment

### 2.1. Sample preparation

#### 2.1.1. Vanadate glasses and glass-ceramics

xNa<sub>2</sub>O•(85-x) V<sub>2</sub>O<sub>5</sub>•10P<sub>2</sub>O<sub>5</sub>•5Fe<sub>2</sub>O<sub>3</sub> and xNa<sub>2</sub>O•(85-x) V<sub>2</sub>O<sub>5</sub>•10P<sub>2</sub>O<sub>5</sub>•5SnO<sub>2</sub> (x=5, 25 and 45 mol%) glasses respectively denoted as xFeV and xSnV were prepared by a conventional melt-quenching method. The mixture of chemical reagents of Na<sub>2</sub>CO<sub>3</sub>(199-01585, Wako), V<sub>2</sub>O<sub>5</sub>(226-00125, Wako), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>(012-03305, Wako), Fe<sub>2</sub>O<sub>3</sub>(096-04825, Wako) and SnO (205-01612, Wako) was placed into a platinum crucible and melted at 1200 °C for 1 h in an electric furnace (NHK-170, Nitto). Dark-brown glass samples were obtained by quenching the crucible bottom with ice-cold water. For the <sup>57</sup>Fe-Mössbauer measurement, 10 mg of <sup>57</sup>Fe<sub>2</sub>O<sub>3</sub> (<sup>57</sup>Fe: 95.90%, ISOFLEX USA) was added to Fe<sub>2</sub>O<sub>3</sub> for the preparation of xFeV glasses. Additionally, each glass sample was heat-treated at 500 °C for 100 min in an electrical furnace to prepare glass-ceramics samples.

#### 2.1.2 Na-ion battery

Na-ion battery was assembled in the type of CR2032, in which Ti- and Ni- mesh fixed the active materials at the cathode and the anode. A separator separated them, and the inside space of the coin cell was filled with electrolyte

(LIPASTE-P/S1, NaClO<sub>4</sub> 1mol/L Propylene Carbonate solution, Tomypure). The cathode of the Na-ion battery was prepared in the mass ratio of  $x\text{FeV}$  or  $x\text{SnV}$  glass and glass-ceramics: acetylene black (ab, 06-0025, Strem Chemicals) to polytetrafluoroethylene (PTFE) as 70:25:5. For the preparation, first, the finely pulverized  $x\text{FeV}$  or  $x\text{SnV}$  glass/glass-ceramics powder and ab with the respective weight of 500 and 178 mg were mixed with a zirconia planetary ball mill (Planet Min(-F), Nagano) under 900 r.p.m for 30 min. The cathode with a weight of 30 mg in 1 cm diameter was formed by pressing 95 mg of the mixture after adding 5 mg of PTFE. Next, an anode was prepared with 30 mg metallic Na (750-70852, Wako) with the same dimension.

## 2.2. Characterization

### 2.2.1. X-ray diffraction

RINT-TTR III diffractometer measured the X-ray diffraction (XRD) patterns (Rigaku) using Cu-K $\alpha$  X-ray ( $\lambda = 0.1581$  nm) generated by setting the tube voltage and current at 50 kV and 300 mA, respectively. The XRD patterns were recorded between  $2\theta$  of 10 and 80° at a scan speed of 5° min<sup>-1</sup> and sampling width of 0.02°. The analysis of the XRD patterns was carried out by PDXL2 ver.2.8.1 using the database ICDD PDF-4.

### 2.2.2. X-ray absorption fine structure (XAFS)

X-ray absorption spectra (XANES / EXAFS) measurements around the vanadium  $K$ -edge were carried out in transmission mode using a beamline BL-12C at the High Energy Accelerator Research Organization (KEK-PF, 1-1 Oh-ho, Tsukuba, Ibaraki, 3050801, Japan). The X-ray beam from the synchrotron was monochromatized by Si (111) double-crystal and cut the higher harmonic waves by Ni mirror. The X-ray intensity was recorded by setting ionization chambers before and after the transmission. The front chamber was filled with N<sub>2</sub>+He gas (N<sub>2</sub>: 30%, He: 70 %), while the rear was with Ar+N<sub>2</sub> gas (Ar:30 %, N<sub>2</sub>: 70 %). A pellet with 0.8 cm in diameter was prepared by pressing the mixture composed of a 5 mg powdered sample and 95 mg boron nitride at 5 kN. The software "Athena version:0.9.26" was used to analyze obtained spectra.

### 2.2.3. <sup>57</sup>Fe- and <sup>119</sup>Sn Mössbauer spectroscopies

<sup>57</sup>Fe- and <sup>119</sup>Sn- Mössbauer spectra of glasses and glass-ceramics samples were measured at room temperature by the conventional constant acceleration method in transmission mode. <sup>57</sup>Co in Rh matrix with the activity of 925 MBq (MCo7. 123, produced on Oct. 1, 2018, Ritverc), and <sup>119m</sup>Sn in CaSnO<sub>3</sub> with 185 MBq (MSn9. 222, produced on Jul. 22, 2015, Ritverc) were used for the sources, while  $\alpha$ -Fe and BaSnO<sub>3</sub> served for the reference of isomer shifts, respectively. The movement of the sources was controlled by a Mössbauer velocity transducer (MVT-1000, Wissel) connected with a digital function generator (DFG-1000, Wissel) and Mössbauer driving unit (MDU-1200, Wissel). The  $\gamma$ -ray signals from the source through the sample were detected by the proportional counter (454131, LND) and amplified by a preamplifier (142IH, ORTEC) and an amplifier (485, ORTEC), which was applied by 2 kV by high voltage power supply (510, ORTEC). The amplified signals were monitored by a

personal computer attached to a single-channel analyzer (SCA-550, ORTEC) and multi-channel scaler (EASY-MCS, ORTEC). Mösswinn 4.0 analyzed the obtained spectra by Lorentzian fitting.

### 2.2.4. Differential thermal analysis (DTA)

Differential thermal analysis (DTA) measurements were performed by Thermo plus TG8120, Rigaku, under the heating rate of 10 K min<sup>-1</sup> and the temperature range between 100 and 600 °C. The weight of the glass sample and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reference was fixed to be 10 mg.

### 2.2.5. Electrical Conductivity

Both DC and AC conductivity measurements were carried out to evaluate the electrical property of the glass samples. The DC conductivity was measured by the four-probe method using DC current-voltage monitor (6241A, ADC). The resistance ( $R$ ) was evaluated by measuring voltage ( $V$ ) by changing current ( $I$ ) from -0.3 to 0.3 mA. The value ( $R$ ) can be calculated from the slope of the  $V-I$  plot, which obeys Ohm's law:

$$R = V / I \quad (1)$$

The conductivity ( $\sigma$ ) was calculated from the relation

$$\sigma = l / (A R) \quad (2)$$

where  $l$  and  $A$  are the sample's longitudinal length (in cm) and cross-section (in cm<sup>2</sup>), respectively. AC conductivity was measured by an impedance analyzer (Alpha-AN Dielectric Spectrometer, Novocontrol Tech.) in the frequency range from 10<sup>-2</sup> to 10<sup>6</sup> Hz and at a temperature from 30 to 150 °C with 20 °C steps. The impedance spectrum at each temperature was measured twice. The specimens were prepared as 5 mm in diameter and 1 mm in thick disk by applying a pressure of 2×10<sup>3</sup> kg to the powdered glass samples. Gold electrodes 3.8 mm in diameter were sputtered onto both sides of the disk using Sputter coater SC7620, Quorum Technologies for the electrical contact.

### 2.2.6. Na-ion battery performance

The charge-discharge capacity and recyclability of the Na-ion battery were measured by a constant current providing device (TOSCAT-3100SK, Toyo-system) in the voltage range between 0.8 and 3.6 V and a current density of 0.2 mA cm<sup>-2</sup> (= 0.15 mA g<sup>-1</sup>) and 2 mA cm<sup>-2</sup> (=1.5 mA g<sup>-1</sup>) at 25 °C. The charge-discharge process was repeated up to 30 times, including 10 min breaks between the charge and discharge processes.

## 3 Results and Discussion

From DTA curves, gradual decreases in glass transition temperature ( $T_g$ ) from 266 to 201 °C and in crystallization temperature ( $T_c$ ) from 343 to 260 °C were observed for  $x\text{FeV}$  glasses as 'x' increased from 5 to 45 mol%. The same behaviour, i.e. decrease of  $T_g$  from 244 to 202 °C, and decrease of  $T_c$  from 307 to 252°C with increasing 'x' from 5 to 45 mol% observed for  $x\text{SnV}$  glass-ceramics. This indicates that the introduction of Na<sub>2</sub>O reduces thermal stability. Furthermore, the DC conductivity at 303K for  $x\text{FeV}$  and  $x\text{SnV}$  glasses and glass-ceramics nanocomposite, before heat treatment, decreases from  $2.82 \times 10^{-5}$  to  $6.61 \times 10^{-7}$  S cm<sup>-1</sup> and from  $1.26 \times 10^{-5}$

to  $4.27 \times 10^{-7} \text{ S cm}^{-1}$ , respectively, with increasing  $\text{Na}_2\text{O}$  content from 5 to 45 mol%. The values of electrical conductivity of  $x\text{FeV}$  and  $x\text{SnV}$  glasses and glass-ceramics nanocomposite are higher than in  $x\text{Na}_2\text{O} \cdot 10\text{P}_2\text{O}_5 \cdot (90-x)\text{V}_2\text{O}_5$ , abbreviated as  $x\text{V}$  glasses, where the electrical conductivity of  $x\text{V}$  decreased from  $5.13 \times 10^{-6}$  to  $9.55 \times 10^{-8} \text{ S cm}^{-1}$  with increasing  $\text{Na}_2\text{O}$  content from 5 to 45 mol%. This indicates that the introduction of  $\text{Fe}_2\text{O}_3$  and  $\text{SnO}_2$  produces an increase in electrical conductivity.  $^{57}\text{Fe}$ -Mössbauer spectra of  $x\text{FeV}$  glass could be described by one doublet and showed a constant isomer shift of  $0.25 \text{ mm s}^{-1}$  and decreasing quadrupole splitting from  $0.73$  to  $0.63 \text{ mm s}^{-1}$ , indicating that  $\text{Fe}^{\text{III}}$  ion forms less distorted tetrahedra upon increasing 'x' from 5 to 45 mol%.  $^{119}\text{Sn}$ -Mössbauer spectra of  $x\text{SnV}$  glass-ceramics nanocomposite, containing also only one doublet, showed an isomer shift increasing from  $0.033$  to  $0.077 \text{ mm s}^{-1}$  and decreasing quadrupole splitting value from  $0.526$  to  $0.520 \text{ mm s}^{-1}$ , with increasing 'x' from 5 to 45 mol%. Additionally, a high capacity of about  $200 \text{ mAh g}^{-1}$  was achieved for the SIB made of  $5\text{FeV}$  glasses as a cathode. This capacity was larger than the previously reported value of  $158 \text{ mAh g}^{-1}$  in  $\text{Na}_{1.25}\text{V}_3\text{O}_8$ . In particular, the high capacity was maintained for up to 30 recharging cycles. The same changes were observed in the  $x\text{SnV}$  glass-ceramics nanocomposite. Therefore, it can be concluded that the introduction of Fe or Sn ions into the phospho-vanadate glass as a cathode causes an increase in durability and conductivity, so these glasses can be considered promising for a high-performance cathode active material with significant improvement of cyclability in sodium-ion batteries.

#### 4 Conclusion

Sodium Vanadate Phosphate glasses with the addition of iron or tin oxides and their glass and glass-ceramics nanocomposite of the composition of  $x\text{Na}_2\text{O} \cdot (85-x)\text{V}_2\text{O}_5 \cdot 10\text{P}_2\text{O}_5 \cdot 5\text{Fe}_2\text{O}_3$  and  $x\text{Na}_2\text{O} \cdot (85-x)\text{V}_2\text{O}_5 \cdot 10\text{P}_2\text{O}_5 \cdot 5\text{SnO}_2$  ( $x=5, 25$  and  $45$  mol%) were investigated in as prepared and heat-treated form by different techniques as DTA, XRD, Mössbauer spectroscopy, DC four-probe method and charge-discharge capacity. The DTA study of  $x\text{FeV}$  and  $x\text{SnV}$  glasses with increasing  $\text{Na}_2\text{O}$  content from 5 to 45 mol% showed a decrease in crystallization temperature ( $T_c$ ) and glass transition temperature ( $T_g$ ) with increasing  $\text{Na}_2\text{O}$  content. Meanwhile, the  $T_c$  and  $T_g$  increased for  $x\text{FeV}$  and  $x\text{SnV}$  as compared to  $x\text{V}$ . The  $T_c$  and  $T_g$  were increased after adding  $\text{Fe}_2\text{O}_3$  and  $\text{SnO}_2$  to the previous glasses system ( $x\text{V}$ ). These results indicated that introducing iron and tin increases the thermal stability of the glass network. This indicates that the 3D V-O network basic construction was splitting into  $\text{VO}_5$  and  $\text{VO}_4$  substructures by increasing  $\text{Na}_2\text{O}$  content. XRD study of  $x\text{FeV}$  and  $x\text{SnV}$  showed an amorphous structure similar to previously investigated  $x\text{FeV}$  samples. At the same time, some crystals phases appeared increasingly in  $x\text{SnV}$ , forming glass-ceramics nanocomposite with particle sizes ranging from 28 to 33 nm. The crystallinity increased with increasing  $\text{Na}_2\text{O}$  content. Also, we conclude that the results of XRD of  $x\text{FeV}$

showed that after heat treatment, several crystalline phases formed:  $\text{Na}_{0.282}\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Na}_{0.282}\text{V}_2\text{O}_5$ ,  $\text{Na}_{1.1}\text{V}_3\text{O}_{7.9}$ ,  $\text{NaVO}_3$  and  $\text{Na}_{1.164}\text{V}_3\text{O}_8$ . Also, the crystallite size of  $x\text{FeV}$  glass-ceramics increased from 26 to 39 (nm) with 'x' of 5 to 45 mol%. The crystal size values of  $x\text{SnV}$  glass-ceramics nanocomposite decreased from 37 to 30 (nm), with 'x' of 5 to 25 mol%  $\text{Na}_2\text{O}$  content.  $^{57}\text{Fe}$  Mössbauer spectra of  $x\text{FeV}$  glasses where 5 mol% of  $\text{Fe}_2\text{O}_3$  is substituted for  $\text{V}_2\text{O}_5$  showed a decrease in quadrupole splitting ( $\Delta$ ) with the increase of  $\text{Na}_2\text{O}$  content, indicating a decrease in the distortion of the iron polyhedral.  $^{119}\text{Sn}$  Mössbauer spectra of  $x\text{SnV}$  glass-ceramics nanocomposite where 5 mol% of  $\text{SnO}_2$  is substituted for  $\text{V}_2\text{O}_5$  showed an increase in  $\Delta$  with the increase of  $\text{Na}_2\text{O}$  content, referring to that the structure transforms from tetrahedral to octahedral  $\text{Sn}^{4+}$ . Electrical conductivity for  $x\text{FeV}$  and  $x\text{SnV}$  before heat treatment decreased from  $2.82 \times 10^{-5}$  to  $6.61 \times 10^{-7} \text{ S cm}^{-1}$  and  $1.26 \times 10^{-5}$  to  $4.27 \times 10^{-7} \text{ S cm}^{-1}$  with increasing  $\text{Na}_2\text{O}$  content from 5 to 45 mol%, respectively. While  $5\text{FeV}$  had higher electrical conductivity than any other prepared samples, the electrical conductivity of  $x\text{FeV}$  samples showed decreasing values as the  $\text{Na}_2\text{O}$  content was increased. This result may be attributed to the decrease in  $\text{V}_2\text{O}_5$  content. According to the data obtained from charge and discharge capacity, it is concluded that  $25\text{FeV}$  (BHT),  $5\text{FeV}$  (AHT),  $5\text{SnV}$  (BHT),  $5\text{SnV}$  (AHT) and  $25\text{SnV}$  (BHT) glass and/or glasses-ceramics nanocomposite can be considered good candidates for using as a cathode material for Na-ion batteries because of the large capacity of 142, 110, 162, 103 and 114  $\text{mAh g}^{-1}$  recorded at room temperature after 30 cycles.

#### Acknowledgement

The author (SK) expresses his gratitude for the financial support from the TMU fund for international collaboration and National Grant-in-aid for Scientific Research (23H02070, 15H03882, 23550238).

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