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

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Abstract

To explore novel vanadate formulations, *i.e.* newly effective cathode active material for sodium-ion battery (SIB), relationships among the local structure, electrical conductivity, and cathode performance of $xNa_2O•10P_2O_5•(85-x)V_2O_5•5Fe_2O_3$ and $xNa_2O•10P_2O_5•(85-x)V_2O_5•5SnO_2$ ($5 \leq x \leq 45$ mol%) glasses and glass-ceramics nanocomposite abbreviated as xFeV and xSnV, respectively, were systematically investigated before and after heat treatment at 500 ℃ for 100 min. Measurements of ^{57}Fe- and ^{119}Sn Mössbauer spectra (FeMS, SnMS, respectively), X-ray absorption fine structure (XAFS), X-ray diffraction patterns (XRD), Fourier Transform Infrared spectroscopy (FTIR), differential thermal analysis (DTA), electrochemical impedance spectra (EIS) and charge-discharge capacity were carried out in this study. From DTA curves, decreases in glass transition temperature (T_g) and crystallization temperature (T_c) were observed for xFeV and xSnV glasses as 'x' increased from 5 to 45 mol% Na_2O content. This indicates that the introduction of Na_2O reduces thermal stability. Furthermore, the DC conductivity for xFeV and xSnV glasses and glass-ceramics nanocomposite, decreases from $2.82 • 10^{-5}$ to $6.61 • 10^{-7}$ S cm^{-1} and from $1.26 • 10^{-5}$ to $4.27 • 10^{-7}$ S cm^{-1}, respectively, with increasing Na_2O content from 5 to 45 mol%. The values of electrical conductivity of xFeV and xSnV are higher than that of $xNa_2O•10P_2O_5•(90-x)V_2O_5$, abbreviated as xV glasses. This indicates that the introduction of Fe_2O_3 and SnO_2 produces an increase in electrical conductivity. ^{57}Fe-Mössbauer spectra of xFeV glass showed decreased quadrupole splitting from 0.73 to 0.63 mm s^{-1}, indicating that Fe^{III} ion forms less distorted tetrahedra upon increasing 'x' from 5 to 45 mol%. Additionally, a high capacity of about 200 mAh g^{-1} was achieved for the SIB made of 5FeV glasses as a cathode. This capacity was larger than the previously reported value of 158 mAh g^{-1} in $Na_{1.25}V_3O_8$. 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 SIBs.

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 [1-3]. Although having high performance with a theoretical capacity of 274 mAh $g^{-1}$for $LiCoO_2$ cathode [4], commercially available Li-ion batteries face the crisis of Li and Co scarcities in the future because their abundance in Earth's crust is only about 20 and 25 ppm, respectively [5]. 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^{3+} [6], Ca^{2+} [7], K^+ [8], Mg^{2+} [9] and Na^+ [10]. The Na-ion battery with a theoretical capacity of 235 mAh g^{-1} for $NaCoO_2$ cathode [4] 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 [5]. 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 [11].

A glass containing P_2O_5 as a glass former enters into many technological applications because of many unique properties such as low glass transition temperature (T_g), low melting temperature (T_c) and high electrical conductivity compared to borate, borosilicate and silicate glasses [12,13]. Phosphate glasses are adaptable because their characteristics may be modified by changing their composition, and the features and uses among these glasses were essentially associated with their microstructure. The network of phosphate glasses is mostly polymeric, formed by connections between PO_4 tetrahedra and modified by the host matrix [14,15]. The structure is considered responsible for the chemical endurance of phosphorous glasses, which affects their applicability. Adding modifier oxides, such as transition metal oxides, can improve their characteristics and chemical stability [12]. Several investigations have demonstrated that introducing transition metals (TM) to glasses increases their chemical stability and endurance by substituting moisture-resistant P-O-TM bonds for bridging P-O-P bonds [15]. Also, TM ions may coexist in glass structures in various oxidation states, and electronic transfer between low-and high-valence states can significantly impact semiconducting, magnetic, and electric properties[16,17]. Vanadium pentoxide alone is an excellent conditional network forming oxide composed of corner-sharing VO_4 tetrahedra. As a result, vanadate glasses can contain a high concentration of vanadium. Vanadium pentoxide is introduced into phosphate glass, it is known to have network-modifying properties. This inclines the phosphate network to depolymerize, the longer chains to shorten, and the local structure to reorganize. At high concentrations, V_2O_5 can act as a network former, seamlessly transitioning from a phosphate network to a pure vanadate network with isolated PO_4 tetrahedra [18].

For the development of 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^{-1} [19]. It was reported that vanadate bronze ($M_xV_2O_5$, M: Na^+, Ag^+) showed relatively high cathode performance when applied in a Na-ion battery [20]. For example, the capacity of 62 and 83 mAh g^{-1} was recorded for $Na_{2.46}V_6O_{16}$ and $Na_{0.33}V_2O_5$ under the current density of 1.5 and 0.02 mA g^{-1}, respectively [20]. Also, vanadate glass is a promising cathode material for Na-ion batteries because of the large pore size due to the amorphous structure and the electrical conductivity (σ) of about 10^{-7}~10^{-5} S cm^{-1}. This latter is due to electron hopping between the vanadium ions of different oxidation states [21]. In our previous study, a large initial discharge capacity of 382.3 mAh g^{-1} was recorded for a Li-ion battery which contained $15LiO_2•10Fe_2O_3•20SnO_2• 5P_2O_5•70V_2O_5$ glass cathode with the electrical conductivity (σ) of $7.4•10^{-7}$ S cm^{-1} [14, 15]. Recently, in comparison to equivalent bulk materials, nanostructured semiconductor materials are currently very sophisticated and effective due to smaller crystallite size, restriction impact, and higher surface area [22-24]. Tin oxide, SnO_2, is a primary rutile type tetragonal stage n-type semiconductor. It exhibits excellent clarity straightforwardness in the obvious region, less electrical resistance, and a large energy hole (3.5 eV) [25-27]. It is frequently used in photovoltaic cells, display devices, field impact semiconductors, cathodes, sensors, biomedicine, batteries, and photocatalysis, among other things, because of its unique features [28].

The ^{57}Fe- and ^{119}Sn- Mössbauer spectra of this glass showed that Fe^{III} was substituted at the network forming site of vanadium ions with the isomer shift (δ) of 0.35 mm s^{-1} and quadrupole splitting (Δ) of 0.88 mm s^{-1}, while Sn^{IV} accommodated network modifying sites of Li-ions showing δ of 0.08 mm s^{-1} and Δ of 0.52 mm s^{-1} [29,30]. Recently, Kubuki *et al*. found that Na-ion battery with a cathode of $xNa_2O•(90-x)V_2O_5•10P_2O_5$ glass with 'x' of 5, 25 and 45 mol% showed a large initial capacity of 307, 184 and 258 mAh g^{-1}, respectively, and a small irreversible capacity of 86, 6 and 21 mAh g^{-1} under the current density of 5 mA g^{-1} [31]. *Yan et al.*[32], found that the electrochemical performance of tin dioxide (SnO_2) as anode materials for lithium-ion and sodium-ion batteries is to be improved by (SnO_2) nanoparticle composites with biomass nitrogen-doped carbon microspheres (SNC composite materials) (LIBs). These results imply that vanadate glass can be a better cathode active material for Na-ion batteries if Fe_2O_3 or SnO_2 is introduced.

In this work, a novel vanadium glass and glass-ceramics nanocomposite with high thermal stability and electrical conductivity is used for active materials for SIBs with high capacities. The relationships between local structure, physical properties and cathode-active properties in the Na-ion battery of Fe_2O_3 or SnO_2 substituted Na_2O-V_2O_5-P_2O_5 glass were investigated by DTA, XRD,^{57}Fe- and ^{119}Sn- Mössbauer spectra, XANES, EXAFS, FTIR, DC conductivity and charge-discharge capacity of the SIB.

2. Experimental

2.1. Sample preparation

2.1.1. Vanadate glasses and glass-ceramics

2.2. Characterization

The details of chemical reagents, materials and characterization are listed in the Supporting information.

All practical steps for sample preparation are illustrated in a schematic figure as shown in Figure 1.

2.3. Na-ion battery

Na-ion battery was assembled in the type of CR2032, in which Ti- and Ni- mesh respectively 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, $NaClO_4$ 1mol/L Propylene Carbonate solution, Tomypure). The cathode of the Na-ion battery was prepared in the mass ratio of xFeV or xSnV 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*FeV or *x*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-Japan) under 900 r.p.m for 30 min. The cathode with the 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-Japan) with the same dimension.

2.4. 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^{-2} (= 0.15 mA g^{-1}) and 2 mA cm^{-2} (=1.5 mA g^{-1}) at 25 ℃. The charge-discharge process was repeated up to 30 times, including 10 min breaks between the charge and discharge processes.

3. Results and Discussion

3.1 Structural Characterization

3.1.1 DTA measurements

DTA curves of $xNa_2O•(85-x)V_2O_5•10P_2O_5•5Fe_2O_3$ (xFeV) and $xNa_2O•(85-x)V_2O_5•10P_2O_5•5SnO_2$ (xSnV) glasses with ‘x’ of 5, 25 and 45 mol% are shown in Figure 2 (A), (B) and (C), respectively. DTA curves of $xNa_2O•(90-x)V_2O_5•10P_2O_5$ (xV) are shown together for comparison. The glass transition temperature (T_g) and crystallization temperature (T_c) of *x*V glasses decrease from $235_{\pm 5}$ to $195_{\pm 5}$ ℃, and from $285_{\pm 2}$ to $251_{\pm 2}$ ℃ with an increasing ‘*x*’ from 5 to 45 mol%Na_2O content [21]. On the other hand, the T_g decreased from $266_{\pm 5}$ to $201_{\pm 5}$ ℃ and a decrease of T_c from $343_{\pm 2}$ to $260_{\pm 2}$ ℃ were recorded for the *x*FeV glasses with an increasing ‘x’ from 5 to 45 mol% Na_2O content. A similar change in T_g from $244_{\pm 5}$ to $202_{\pm 5}$ ℃, and T_c from $307_{\pm 2}$ to $252_{\pm 2}$ ℃ were observed for xSnV with an increasing ‘x’ from 5 to 45 mol%. The decreases in T_g and T_c observed for xFeV and xSnV glass and glass-ceramics with the increase of Na_2O content are similar to the trends observed in xV glasses, which was explained by the cleavage of the 3D-glass network formed of VO_4, VO_5, and PO_4 units generated by Na^+ [31]. It is also likely to be due to increased in NBOs, and this has been inferred from the FTIR results that are mentioned in the FTIR section. This is implying to the thermal stability of xFeV and xSnV glass and glass-ceramics were decreased with the introduction of Na^+ in the glass matrix. Notably, the increases of T_g and T_c were observed by the substitution of Fe_2O_3 and SnO_2 for V_2O_5, which shows that the introduction of these oxides can enhance the thermal stability of the vanadate glass. The thermal stability of glass can be evaluated by $(T_c - T_g)$ [Hruby parameter] [33]. The value of $(T_c - T_g)$ increased from 50 to 77 and 63 K for 5FeV and 5SnV, respectively. Similar changes in $(T_c - T_g)$ were observed for 25V (33 K), 25FeV (39 K) and 25SnV (26 K), and for 45V (56 K), 45FeV (59 K) and 45SnV (50 K) - the Hruby parameters are given in the brackets. It can be considered that the thermal stability of xV glasses can be effectively increased by the introduction of Fe_2O_3 and SnO_2 oxides, which reduced NBOs in the glass matrix, so the values of $(T_c - T_g)$ increase compared to the same concentration of Na_2O in xV, which causes an increase in the thermal stability of the samples[30-34], which leads to an improvement in the ability of glass formation for use in sodium-ion batteries. Based on the T_g's and T_c's of xFeV and xSnV glasses, the heat treatment temperature was fixed to be 500 ℃ for 100 min. The changes in structure and physical properties of xFeV and xSnV before and after the heat treatment were examined.

3.1.2. XRD patterns

Figure 3 (A), shows the (XRD) patterns for $xNa_2O{\bullet}(85\text{-}x)V_2O_5{\bullet}10P_2O_5{\bullet}5Fe_2O_3$ (xFeV) glass before heat treatment (BHT), with 'x' of 5, 25 and 45 mol% Na_2O content. The amorphous state of the present samples is confirmed by the broad hump scattering band, which locates at 2Θ in this range (25- 28^o) [35]. On the other hand, Figure 3 (B) and Table 1 show the XRD patterns of 5FeV glass-ceramics nanocomposite after heat treatment, (AHT), at 500 ℃ for 100 min showing intense main peaks with small linewidth observed, this is ascribed to $Na_{0.282}V_2O_5$ crystalline phase (PDF No.: 01-086-4171), and V_2O_5 (PDF No.: 01-086-9697). In the XRD pattern of heat-treated 25FeV glass-ceramics (Fig. 3(B)), peaks were observed due to the $Na_{1.1}V_3O_{7.9}$ crystalline phase (PDF No.: 00-045-0498) together with $Na_{0.282}V_2O_5$ crystalline phase. Meanwhile, the XRD pattern of heat-treated 45FeV glass-ceramics (Fig. 3(B)) shows several peaks attributed to a□$NaVO_3$ crystalline phase (PDF No.: 00-027-0828) and to $Na_{1.164}V_3O_8$(PDF No.: 01-078-2864). Similarly, XRD patterns of xSnV glass-ceramics showed a halo pattern due to the amorphous structure together with intense peaks due to SnO_2 (PDF No.: 01-077-0447) (Figure 4 (A)), while those of the heat-treated samples indicated the presence of $Na_{0.33}V_2O_5$ crystalline phase (PDF No.: 01-073-6271). $Na_{1.164}V_3O_8$ was found in 5SnV glass-ceramics as shown in Fig. 4 (B), and the V_2O_5 crystalline phase (PDF No.:01-077-2418) appeared in 25SnV glass-ceramics. Relevant 2Θ values are summarized in Table 1.

We calculated the crystalline size in glasses xFeV and xSnV after heat treatment by Scherrer's equation [36,37]:

$$D = \frac{0.9\,\lambda}{B\,\cos\Theta} \qquad (1)$$

Where D, B,λ and Θ are the crystallites size, full width at half maximum of diffraction peak, the wavelength of the X-ray source and the diffraction angle for the diffraction line, respectively. Table1 shows the crystallite size of xFeV and xSnV glasses and glass-ceramics before heat treatment. XRD study of xFeV and xSnV showed amorphous structure, just like for previously investigated xFeV samples, while some crystalline phases appeared increasingly in xSnV with 'x' from 5 to 45 mol% Na_2O content forming glass-ceramics nanocomposite with particle size between 28 and 33 nm. The calculated crystal size of xFeV and xSnV after heat treatment at 500 ℃ for 100 min was found in the nanometer (nm) range and changed with increasing Na_2O content. Table 1 shows the crystallite size values of xFeV glass-ceramics nanocomposite increasing from 26 to 39 (nm) with an increase of 'x' from 5 to 45 mol%. Meanwhile, the crystallite size in xSnV glass-ceramics decreased from 37 to 30 (nm), with an increasing 'x' from 5 to 45 mol%. The detected crystalline phases of $Na_{0.282}V_2O_5$, $Na_{1.1}V_3O_{7.9}$ and $Na_{0.33}V_2O_5$ are known as vanadium bronzes. They can be responsible for the high electrical conductivity of 5SnV and 25SnV glass-ceramics samples, as shown in (Figure 4 (B)). Therefore, heat-treated samples 5FeV, 25FeV and 5SnV are promising to be used as a cathode active material for SIB. These crystalline phases are not identified in the heat-treated $xNa_2O \bullet 10P_2O_5 \bullet (90-x)V_2O_5$ glasses (xV) [31]. Therefore, the introduction of Fe_2O_3 or SnO_2 facilitates the formation of vanadium bronze by enhancing its thermal stability [9, 34, 36, 38]. The crystalline phases are not detected from the XRD pattern of 45SnV glass-ceramics because the sample melted after the heat treatment. These results were obtained from XRD patterns before and after heat treatment of xFeV and xSnV glasses and glass-ceramics, confirming previously obtained results from DTA curves. The values of T_g and T_c increase significantly with the increase of Na_2O concentration in the glass network after adding Fe_2O_3 and SnO_2 oxides.

3.1.3. ^{57}Fe- and ^{119}Sn-Mössbauer spectra

Figure 5 shows the Mössbauer spectra of xFeV glasses recorded before and after heat treatment at 500 ℃ for 100 min. ^{57}Fe-Mössbauer spectra of xFeV glasses before heat treatment are displayed in Figure 5(A), shown together with the Mössbauer parameters in Table 2. The Mössbauer isomer shift (δ) for xFeV glass did not depend on the Na_2O content within experimental error. Before heat treatment, Fe ions were homogeneously distributed in the glass matrix because no crystalline phases containing Fe were identified by the corresponding XRD patterns (see Fig.3). The obtained values of δ were smaller than 0.41 mm s^{-1} indicating that iron ions form $Fe^{III}O_4$ tetrahedra (T_d) [9, 26, 29]. At the same time, the quadrupole splitting (Δ) decreased, indicating that the local symmetry of Fe^{3+} (T_d) decreased with the increase of Na_2O content (x) (see Figure 5(A)). As previously shown in Figure 2, values of T_g of xFeV decreased from $266_{\pm 5}$ to $201_{\pm 5}$ ℃, with an increasing 'x' from 5 to 45 mol%. The decrease of (Δ) of Fe^{3+} is due to the production of non-bridging oxygens (NBOs) that increase with increasing Na_2O content [33, 39, 40], referring to the increase in the uniformity of the O-Fe-O angle and Fe-O length in the glass matrix [40].

According to Nishida [31], the gradual decrease in Δ observed from Mössbauer spectra of alkali vanadate glass systems of $xR_2O•(90-x)V_2O_5•10Fe_2O_3$ (R = Na, K and Li) is caused by a structural transition from two-dimensional layered structure composed of V_2O_5 tetragonal pyramids to a one-dimensional network structure of VO_4 tetrahedra [31]. Similarly, xFeV glasses transfer from a two-dimensional layer structure consisting of a V_2O_5 tetragonal pyramid to a one-dimensional chain structure composed of VO_4 tetrahedra with the introduction of Na_2O content. As smaller δ values of $0.39_{\pm 0.01}$, $0.38_{\pm 0.01}$ and $0.26_{\pm 0.01}$ mms^{-1} were obtained for ^{57}Fe-Mössbauer spectra of $xNa_2O•(89-x)V_2O_5•10P_2O_5•^{57}Fe_2O_3$ with 'x' of 5, 25 and 45mol%, respectively [41], it is clear that the substitution of 5 mol% Fe_2O_3 for V_2O_5 in xV glass resulted in the reduction of Fe-O bond covalency.

On the other hand, an increase in δ from $0.333_{\pm 0.001}$ to $0.447_{\pm 0.009}$ mm s^{-1}, and dramatic decrease of Δ from $0.710_{\pm 0.01}$ to $0.318_{\pm 0.05}$ mm s^{-1} and a decrease of Γ from $0.495_{\pm 0.02}$ to $0.265_{\pm 0.05}$ were observed for xFeV glasses after heat-treated at 500 ℃ for 100 min with an increasing 'x' from 5 to 45 mol% as demonstrated in Figure 5 (B) and Table 2. A dramatic decrease in Δ indicates that the Fe^{III}-O chemical bond strength becomes weaker and the distortion of $Fe^{III}O_4$ tetrahedra is reduced because of the structural relaxation caused by the isothermal heat treatment. A concordant shift in the intensity of pre-edge peaks in XANES was seen for xFeV glass before and after the heat treatment, reflecting the improvement in symmetry of VOx polyhedral. After the heat treatment, the local distortion of FeO_4 decreased. No research findings linking iron sites functioning as a probe for vanadate glasses have been published to date. However, one may infer from the Mössbauer and XANES results in the current study that Fe^{3+} serves as a probe for modifications to the vanadate network. From Figures 5 (A and B), we conclude that the decrease in Δ for xFeV is more evident after heat treatment, which enables the samples to gain more thermal energy, effectively reducing the distortion of VO_4 and FeO_4 tetrahedra. Figure 6 (A) depicts the ^{119}Sn-Mössbauer spectra of xSnV recorded at room temperature, shown together with the Mössbauer parameters in Table 2. The values of δ increased from $0.033_{\pm 0.006}$ to $0.077_{\pm 0.001}$ mm s^{-1} for Sn^{4+} ions with an increasing 'x' from 5 to 45 mol%. [33]. The increase in δ values indicates the octahedral Sn^{4+} ions with increasing Na_2O content. The low δ values are due to the more ionic character of Sn^{4+} ions approaching the electronic configuration of $4d^{10}$ [33]. The Δ values of xSnV glass-ceramics decreased from $0.526_{\pm 0.02}$ to $0.520_{\pm 0.003}$ mms^{-1} with increasing Na_2O content, this may indicate that the structure transforms from tetrahedral to octahedral Sn^{4+} [30], however, this decrease is comparable with the experimental error. As shown in Table2, the linewidth (Γ) values at room temperature of xSnV decreased from $1.062_{\pm 0.03}$ to $0.960_{\pm 0.04}$ mm s^{-1} with 'x' from 5 to 45 mol%. A decrease in Γ values of xSnV glass-ceramics shows the increase in the uniformity of the Sn^{4+}- O^{2-} chemical bond. Additionally, an increase in δ from $0.072_{\pm 0.004}$ to $0.231_{\pm 0.008}$ mm s^{-1} and a decrease in Δ from 0.522 $_{\pm 0.01}$ to $0.443_{\pm 0.03}$ mm s^{-1} were observed for xSnV glass-ceramics after heat-treated at 500 ℃ for 100 min as shown in Figure 6 (B). An increase in Γ values of xSnV glass-ceramics from $0.892_{\pm 0.01}$ to $0.956_{\pm 0.04}$ refers to the increased crystallinity of the internal structure after heat treatment. Mössbauer parameters are not shown for 45SnV glass because the sample melted after the heat treatment.

3.1.4. XANES and EXAFS spectra

For determining the valence states changes of vanadium in these glass materials, XANES spectra were recorded for the samples xFeV. Figure 7 (A and B) depicts the x-ray absorption near V *K*-edge spectra, and Fourier transforms of V *K*-edge EXAFS (FT- EXAFS) of xFeV with 'x' from 5 to 25 and 45 mol% of Na_2O before and after heat treatment at 500 ℃ for 100 min together with spectra of V_2O_5 and V foils. Figure 7 (A) shows the normalization spectra of a pre-edge peak of V-*K* for V foils and V_2O_5 observed at 5463 and 5468 eV, as well as that of xFeV glasses at 5468 eV. The intensity of the normalized absorbance ($E_{0.5}$) was observed to increase before heat treatment with increasing Na_2O content. We know that the pre-edge peaks have been attributed to 1s – 3d electronic-forbidden transitions [31]. It represents the level of oxygen atom distortion in the first coordination, which is influenced by the degree of orbital hybridization between the 2p and 3d. [31]. On the other hand, after heat treatment, all pre-edge peaks are remarkably similar after the crystallization of the xFeV glasses. In (Figure 7 (B)), we see the XANES spectrum of xFeV glass after heat treatment, noting that the pre-edge values did not change compared to the values of xFeV before heat treatment. As shown in Figure 7 (A), the absorption peak of Vanadium metal (V foil), xFeV with ‘x’ from 5 to 25 and 45 mol% and V_2O_5 show up at 5471, 5477, 5478, 5479 and 5480 eV, respectively.

Figure 8, shows the V K-edge EXAFS (FT-EXAFS) for xFeV glasses before and after heat treatment are shown together with that of V_2O_5 and V foil. Figure 8 (A), shows the peaks of the xFeV before heat treatment. These peaks located at 0.82 Å, 1.12 Å, 1.62 Å and 2.79 Å were attributed to V_2O_5. From Figure 8 (A), note that the peak at 0.82 Å for V_2O_5 disappeared in xFeV, but the peak at 1.2 Å was present in 5FeV at 1.12 Å, in 25FeV at 1.16 Å, and in 45FeV at 1.24 Å, it shifts towards higher values with increasing ‘x’ from 5 to 25 and 45 mol%. Meanwhile, the absorption peaks of metallic V appear at 0.87 Å, 2.3 Å, 3.8 Å and 4.7 Å as shown in Figure 8 (A). The peaks of xFeV after heat treatment are shown in Figure 8 (B). The peaks located at 0.82 Å, 1.12 Å, 1.62 Å and 2.79 Å were attributed to V_2O_5. The distorted VO_6 octahedron of the V_2O_5 crystal has V-O distances of 1.6 Å, 1.8 Å, 1.9 Å, 2.0 Å and 2.8 Å [31]. The shoulder at 2.8 Å is due to V-V correlations at ~3.2 Å [31]. The most prominent peak at 1.62 Å in the figure is related to V-O bond lengths of 1.9 and 2.1 Å. On the other hand, the FT curve of V foils showed peaks at 0.9 Å, 1.2 Å, 1.45 Å, and 2.4 Å. [34].

Figure 8(A) shows the FT-EXAFS curves of xFeV glasses which differ from V_2O_5 and metallic V. The short V=O double bonds, which peaked at 0.7 Å in Figure 8(A), and the main peak at 1.6 Å, are also present in the glass. The majority of V-O bonds of the glasses are seen at the peaks at 1.4 Å. There are possibly a few longer distances at 2.85 Å. Also, the shortest sharp V-V peak is not detected in the FT curves of the glasses. After crystallization Figure 8 (B), the structural units of *x*FeV glasses change clearly. The peak at 2.73 Å in the 5FeV sample increasingly resembles V_2O_5 and the same can be confirmed from their XRD patterns. Also, for 25FeV and

45FeV glass-ceramics nanocomposite obtained after heat treatment, the peak intensity is increased compared to 5FeV glass. As a result, it could be said that the FT- EXAFS results and the XRD study demonstrating the crystallinity of these nanocomposites are in good agreement.

3.1.5. FTIR Spectra

FTIR spectroscopy is essentially an analytical technique for understanding the composition of various materials. FTIR transmission spectra of xFeV and xSnV glasses and glass-ceramics before and after heat treatment at 500 ℃ for 100 min are shown in Figure 9, (**Table S1 and Table S2**). A small peak is located in the range (1638 -1633) cm^{-1} in xFeV before heat treatment, (BHT), also this peak is positioned in the range (1634 -1639) cm^{-1} in xFeV after heat treatment, (AHT), with ‘x’ increase from 5 to 45mol.% Na_2O, this peak is attributed to the hydroxyl group(OH^-) [35]. A small peak was observed in range (1370-1373) cm^{-1} in xFeV (BHT), and (1378-1369) cm^{-1} in xFeV (AHT) ‘x’ increase from 5 to 45mol.%, is ascribed to vibration of non-bridging (PO_2) [33,36,41]. The intensity of this peak was increased with increasing Na_2O content, indicating an increase in NBOs in the glass network. It is known that an increase in NBOs in the glass network leads to an open structure, and leads to a decrease in T_g of glass samples [33,42]. These results are in good agreement with the DTA results. Moreover, the absorption peak observed at 1206 cm^{-1} in xFeV (BHT), and at 1193 cm^{-1} in xFeV (AHT) is attributed to P-O stretching mode [33,41], **Table S1** shows this peak was shifted to a lower wavenumber and Figure 9(A, B), shows the intensity of this peak increases with increasing Na_2O content. Also, the absorption peaks in this range (1006-1064) cm^{-1} of xFeV before and after heat treatment are ascribed to the V=O stretching mode of the VO_5 pyramid [33,42], the intensities of the peaks were increased with increased ‘x’ from 5 to 45mol.% Na_2O as shown in Figure 9(A, B). As well as, the absorption peaks in the range (933-994) cm^{-1} of xFeV before and after heat treatment attributed to the VO_3 terminal stretching mode of pyrovanadate ($V_2O_7^{4-}$) ion [41]. The absorption peak located at 758 cm^{-1} in 5FeV(BHT), at 760 cm^{-1} in 25FeV(BHT), and did not appear in 45FeV(BHT) glasses, while this peak was only appeared at 763 cm^{-1} in 25FeV(AHT), this peak is assigned to V-O stretching mode of $V(T_d)O_4$ [33,41]. The absorption peak located at 688 cm^{-1} in xFeV (BHT) was shifted to a lower wavenumber and the intensity of the peak was increased with increasing Na_2O content, while this peak only appeared in 45FeV (AHT). This peak is attributed to the V-O-V anti-symmetric stretching mode [41]. Moreover, the absorption peak located at 546 cm^{-1} may be attributed to the

P-O-P bending and Fe-O stretching mode of Fe(T_d)O_4 [33,36,41]. The results are in good agreement with the results obtained by Mössbauer spectroscopy. The small peak was observed in the range (459- 476) cm^{-1} in xFeV(BHT) and (478-474) cm^{-1} in xFeV(BHT), assigned to bending unite in PO_4 tetrahedron [33, 42].

On the other hand, the FTIR absorption peaks of xSnV before and after heat treatment are shown in Figure 9(C, D) and **Table S2**. The absorption peaks of xSnV glasses and glass-ceramics were observed at 443 cm^{-1} in xSnV (BHT) and at 473 cm^{-1} in xSnV (AHT) are may be ascribed to bending unit of PO_4 tetrahedra [**33, 42**], at 535 cm^{-1} in xSnV (BHT) and at 537 cm^{-1} in xSnV (AHT) may be attributed to P-O-P bending [**33,36,41**], at 633 cm^{-1} in xSnV (BHT) and at 652 cm^{-1} in xSnV (AHT) to V-O-V anti-symmetric stretching mode[41,42] at 738 cm^{-1} in 45SnV (BHT) and at 755 cm^{-1} in 5SnV (AHT) to V-O stretching mode of V(T_d)O_4 [**33,41**], at 828 to 863 cm^{-1} in xSnV (BHT) and at 817 to 838 cm^{-1} in xSnV (AHT) to P-O-P groups[**33**, **42**], at 944 to 997 cm^{-1} in xFeV (BHT) and at 949 cm^{-1} in 5SnV (AHT) to VO_3 terminal stretching mode of pyrovanadate ($V_2O_7^{4-}$) ion, at 1006 cm^{-1} in xSnV (BHT) and at 1016 cm^{-1} in xSnV (AHT) [**33,36,41**], 1064 cm^{-1} in xSnV (BHT) and at 1065 cm^{-1} in xSnV (AHT) to V=O stretching mode of VO_5 pyramid [**36,42**]. Moreover, the absorption peak observed at 1205 cm^{-1} in xSnV (BHT), and at 1218 cm^{-1} in xSnV (AHT) is attributed to P-O stretching mode [**33,41**], **Table S2** shows this peak was shifted to a lower wavenumber and Figure 9(C, D), shows the intensity of this peak increases with increasing Na_2O content. A small peak was observed in range (1370-1373) cm^{-1} in xSnV(BHT), and (1378-1369) cm^{-1} in xSnV (AHT) 'x' increase from 5 to 45mol.%, is ascribed to vibration of non-bridging (PO_2) [33,36,41]. The intensity of this peak was increased with increasing Na_2O content, indicating an increase in NBOs in the glass network. It is known that an increase in NBOs in the glass network leads to an open structure, and leads to a decrease in T_g of glass samples [33,42]. A small peak is located in this range (1638 -1633 cm^{-1}) in xSnV before heat treatment, (BHT), also this peak is positioned in the range (1634 -1639) cm^{-1} in xSnV after heat treatment, (AHT), with 'x' increase from 5 to 45mol.% Na_2O, this peak is attributed to a hydroxyl group$(OH)^-$ [35].

According to the FTIR study, xFeV and xSnV glasses and glass-ceramic samples are considered to be formed of PO_4 tetrahedra with P-O-P bonds to form a 3D-network structure, in which tetrahedral Fe^{3+} ions form P-O-Fe bonds. Since stretching or vibrational mode was seen in the FTIR spectra, it is important to emphasize that Tin functions as a network modulator in the glass matrix. By breaking the P-O-P bonds and forming ionic connections with NBO atoms, tin is thought to function as a network modifier (NWM). These results are in good agreement with the DTA results.

3.2. Electrical Conductivity

The conductivity spectra at different temperatures for 5FeV, 25FeV, 5SnV and 25SnV glasses are shown in **Figure 10 (a,b)** and **Figure S1(a,b)**. Similar conductivity spectra are obtained for 5V and 25 V glasses free of Fe_2O_3 and SnO_2. As can be seen from the figure, for all samples and at all temperatures, conductivity isotherms are frequency-independent (σ_{DC}) over nearly the entire experimental frequency range indicating fast electronic transport. None of the conductivity spectra shown in **Figure 10** exhibits a decrease in conductivity at low frequencies, a feature known as the electrode polarization effect arising from the blocking of ions at the metallic electrodes [31, 34, 43]. This signifies that the mobility of sodium ions in xFeV and xSnV glasses with x ≤ 25 mol% is very low and that the dominant conductivity mechanism in these glasses is naturally electronic (polaronic). On the other hand, conductivity spectra at room temperature for 45FeV, 45SnV and 45V glasses exhibit the electrode polarization effect, as seen from the low-frequency region in **Figure 11**. This implies that in these three samples, ionic transport is the significant if not the main conductivity mechanism. Also, it is worth noting that the conductivity spectra of these glasses show an increase of conductivity with an increasing frequency above 10 kHz which originates from the correlated short-range hopping of charge carriers [44], *i.e.* mobile sodium ions.

With increasing temperature, the conductivity of xFeV, xSnV, and xV glasses with x ≤ 25 mol% increases, showing a linear dependence of $\log(\sigma_{DC}T)$ vs. 1000/T, see **Figure 12**. From the slope of these lines, the values of DC activation energies, E_{DC}, were calculated using the equation [44]:

$$\sigma_{DC}T = \sigma_0 \exp(E_{DC}/k_BT) \qquad (2)$$

where k_B is Boltzmann's constant and σ_0 is the pre-exponential factor. The E_{DC} values and σ_{DC} at 30 °C for all samples are listed in **Table 3** and shown in **Figure 13**. The electrical conductivity of the glasses within all three series decreases continuously with increasing Na_2O content up to 45 mol%, as seen in **Figure 13**. On the other hand, the E_{DC} exhibits increases as the Na_2O increases up to 25 mol%, see **Table 3**. The observed trends in σ_{DC} and E_{DC} are interesting in several aspects.

For one, the decrease in conductivity in all three series is related to the decrease in V_2O_5 content and hence the decrease in electronic transport contribution to the total conductivity. The glasses containing high amounts of vanadate oxide with a constant amount of Fe_2O_3 and SnO_2 are well-known polaronic conductors [41, 45-47]. Our results clearly show that introducing sodium ions cannot compensate for the decrease in electronic transport associated with the decrease in the concentration of vanadium ions. Also, it is noteworthy to observe that the trend in conductivity is consistent with the decrease of T_g and T_c as shown in **Figure 2**, since the glass network structure weakens by the gradual increase in Na_2O, preventing the polaronic transport via V^{4+}-V^{5+}, Sn^{3+}-Sn^{4+} and Fe^{2+}-Fe^{3+} ions [33, 41, 45,48]. For two, it is remarkable to observe that for each concentration of Na_2O, the conductivity of glasses free of Fe_2O_3 and SnO_2 is the lowest and for glasses containing Fe_2O_3 is the highest with glasses containing SnO_2 being mostly in the middle, see Figure 13. The conductivity change for each concentration of Na_2O spans nearly one order of magnitude. This result implies that the substitution of 5 mol% of V_2O_5 by either Fe_2O_3 or SnO_2 positively impacts electronic transport, stimulating polaron hopping most likely between various TM ions, for instance, V^{4+}-Sn^{3+} or V^{4+}-Fe^{3+}. Here, iron ions appear to have a more positive influence than tin ones, which could be related to the Mössbauer parameters, as shown in Table 2. Eventually, for the highest fraction of Na_2O (45 mol%), the conductivity of 45FeV and 45SnV glasses are very similar due to the small contribution of polaronic transport, and predominance of sodium ion dynamics.

Finally, it should be noted that no influence of the crystalline phase(s) detected by XRD in 5SnV and 45SnV glass-ceramics, see Figure 4 and related discussion, on the electrical transport was observed from conductivity spectra. That is conductivity spectra of these samples do not show any additional frequency-dependent features in the middle-frequency range, which might point towards the electrical relaxation inside or at the boundaries of the crystalline grains. This result suggests that the crystalline grains are randomly distributed and disconnected, so the electrical transport interruptedly occurs in the continuous glassy matrix.

3.3. Charge-Discharge capacity

Charge-discharge capacity loops of xFeV and xSnV glasses and glass-ceramics nanocomposite before and after heat treatment with increasing Na_2O content from 5mol% to 45mol.% were recorded 30 times, as displayed in Figures 14, 15, (S2 and S3). Before the heat treatment, the initial capacity and irreversible capacity for xFeV glasses were found at 97, 118 and 83 mAhg^{-1} as well as 19, 22 and 15 mAhg^{-1} for 5FeV, 25FeV and 45FeV glasses in 10 cycles as shown in Figure 14 (A) and (Figure S2). Figure 14 (B) and (Figure S2) show charge-discharge capacity loops for heat-treated xFeV glasses recorded in 10 cycles, and the capacities were found to be 119, 83 and 82 mAhg^{-1} as well as 22, 16 and 15mAhg^{-1} for 5FeV, 25FeV and 45FeV glass-ceramics nanocomposite, respectively. The initial capacity and irreversible capacity of xSnV glass-ceramics before heat treatment were found at 83, 83 and 82 mAhg^{-1} as well as 22, 15 and 16 mAhg^{-1} for 5SnV, 25SnV and 45SnV glass-ceramics, respectively, as shown in Figure 15 (A) and (Figure S3) recorded in 10 cycles. Figure 15 (B) and (Figure S3) show the initial capacity and irreversible capacity for xSnV recorded in 10 cycles being 118, 117 and 116 mAhg^{-1} as well as 23, 24 and 24 mAhg^{-1} for 5SnV, 25SnV and 45SnV glass-ceramics nanocomposite, respectively. According to *A. Langrock, et al.* [37], the high irreversible capacity of 75 mAhg^{-1} was recorded for Na_2FePO_4F. We affirmed that an irreversible capacity of 22 mAhg^{-1} was recorded for 5FeV glass, whereas this value decreases significantly at 45FeV to 15 mAhg^{-1}. Also, the same behaviour occurred with the xSnV glass-ceramics nanocomposite when the Na_2O was increased, the irreversible capacity has been reduced from 22 mAhg^{-1} (x=5) to 16 mAhg^{-1} (x=45). This result shows that adding Na^+ as a modifier to the V_2O_5•P_2O_5•Fe_2O_3 and V_2O_5•P_2O_5•SnO_2 glass and glass-ceramics series leads to a decrease in the irreversible capacity [50]. Therefore, it will play an important role in the improvement of the performance of the secondary Na-ions battery when xFeV glass and xSnV glass-ceramics nanocomposite are applied as a cathode. Table S3 shows the values of the irreversible and initial capacities for xV, xFeV and xSnV from 5mol% to 45 mol% Na_2O content. The irreversible and initial capacity for, xV, xFeV and xSnV decreases with increasing Na_2O content. The higher values of the irreversible and initial capacity of xV, xFeV and xSnV samples were observed at x=5 mol % Na_2O content. On the other hand, the irreversible and initial capacity of xFeV is higher than those of xSnV before heat treatment confirming the DC electrical conductivity results. As shown in (Table S3) the irreversible and initial capacities decreased in our present samples xFeV and xSnV in comparison with xV samples [21]. Based on this result, charge-discharge capacity evaluation of Na-ions battery taking place at a higher current density of 1.5 mA cm^{-2} was carried out for the xFeV glasses and xSnV glass-ceramics nanocomposite at room temperature.

3.4. Cyclability and Stability

The discharge capacities of xFeV and xSnV before and after heat treatment with increasing Na_2O content from 5mol% to 45mol.% recorded at room temperature were measured up to 30 cycles as presented in Figure 16 (A, B). A gradual decrease in capacity with an increasing number of cycles is observed with increasing the Na_2O content. From the data in Table. 4, one can see that the initial capacity after adding Fe_2O_3 and SnO_2 to the base glass system is higher than that of xV, at 5 mol.% Na_2O content. Figure 16 (A) shows the initial capacity of xFeV before heat treatment and after heat treatment, (abbreviated as (BHT) and (AHT)), observed as 101, 110, 142, 84, 8 and 30 mAh g^{-1} for 5FeV (BHT), 5FeV (AHT), 25FeV (BHT), 25FeV (AHT), 45FeV (BHT) and 45FeV (AHT), respectively. Also, the capacity of *x*SnV after 30 cycles gradually decreased being 80, 77, 66, 30, 4 and 9 mAh g^{-1} for 5FeV (BHT), 5FeV (AHT), 25FeV (BHT), 25FeV (AHT), 45FeV (BHT) and 45FeV (AHT), respectively. The maintenance rate (%) of xFeV after 30 cycles was 78.2, 69, 46.4, 36.9, 50 and 26.6 % for 5FeV (BHT), 5FeV (AHT), 25FeV (BHT), 25FeV (AHT), 45FeV (AHT) and 45FeV (BHT), respectively. It is noticed that the glass samples containing 5 and 25 mol% Na_2O before and after heat treatment have the largest capacity as well as the highest maintenance rate (%) of xFeV after 30 cycles. Therefore, the glasses samples, 5FeV (BHT) and 5FeV (AHT) and 25FeV (BHT) are promising samples to be used as cathodes in SIB.

In Figure 16 (B) the initial capacities of xSnV before and after heat treatment were detected as 162, 103, 114, 98, 9 and 3 mAh g^{-1} for 5SnV (BHT), 5SnV (AHT) 25SnV (BHT), 25SnV (AHT), 45SnV (BHT) and 45SnV (AHT), respectively. Also, the capacity of xSnV after 30 cycles gradually decreased. The measured values were found 106, 96, 63, 70, 5 and 2 mAh g^{-1} for 5SnV (BHT), 5SnV (AHT) 25SnV (BHT), 25SnV (AHT), 45SnV (BHT) and 45SnV (AHT), respectively. The maintenance rate (%) of *x*FeV after 30 cycles was 65.4, 93.2, 55.2, 71.4, 55.5 and 67% for 5SnV (BHT), 25SnV (BHT), 5SnV (AHT), 25SnV (AHT), 45SnV (BHT) and 45SnV (AHT), respectively. Likewise, the glass samples containing 5 and 25 mol% Na_2O before and after heat treatment have the largest capacity as well as the highest maintenance rate (%) of *x*SnV after 30 cycles. Hence, the glass-ceramics nanocomposite samples, 5SnV (BHT), 5SnV (AHT), 25SnV (BHT) and 25SnV (AHT) are also considered promising to use as cathode in SIB. From Table 4, an increase in the capacity values is noticed as Fe or Sn was added to xV samples, especially at x=5 and 25 mol.% Na_2O content. This increase in capacity after adding Fe_2O_3 or SnO_2 oxides to the xV glasses network indicates that Fe and Sn ions improve the capacity and the cyclability. In Table 4, data on some cathodes containing sodium, vanadium and iron are presented for comparison: the highest capacity is shown with the number of cycles as well as the current density applied. Finally, one can see that the samples 5FeV (BHT), 5FeV (AHT), 25SnV (BHT) and 25SnV (AHT) are considered promising for application as a cathode in SIB because there is no drop in the capacity value after 30 cycles. By Comparing the capacity values of 115 mAh g^{-1} recorded for $Na_4 Fe_3 (PO_4)_2 P_2O_7$ [51] and 75 mAh g^{-1} for Na_2FePO_4F [46] by our results, one can say that our samples are considered promising for more studies in this field. It can be concluded that 5FeV (BHT), 5FeV (AHT), 25FeV (BHT), 5SnV (BHT), 5SnV (AHT) and 25SnV (BHT) glasses and/or glass-ceramics nanocomposite have the possibility of being used as a cathode active material of SIB because it shows a large initial capacity value 101, 110, 142, 162, 103 and 114 mAh g^{-1}, respectively.

Conclusion

Sodium Vanadate Phosphate glasses with the addition of iron or tin oxides and their glass and glass-ceramics nanocomposite of the composition of xFeV and xSnV were investigated in as prepared and heat-treated. The DTA study of xFeV and xSnV glasses with increasing Na_2O content from 5 to 45 mol% showed a decrease in crystallization temperature (T_c) and glass transition temperature (T_g) with increasing Na_2O content. The T_c and T_g were increased after adding Fe_2O_3 and SnO_2 to the previously glasses system (xV). These results indicated that the introduction of Fe and Sn increases the thermal stability of the glass network. XRD study of xFeV and xSnV showed amorphous structure, similarly to previously investigated xFeV samples, while some crystalline phases appeared increasingly in xSnV forming glass-ceramics nanocomposite. We can conclude that the results of XRD of xFeV showed that after heat treatment, several crystalline phases formed $Na_{0.282}V_2O_5$, V_2O_5, $Na_{0.282}V_2O_5$, $Na_{1.1}V_3O_{7.9}$, $NaVO_3$ and $Na_{1.164}V_3O_8$. ^{57}Fe Mössbauer spectra of xFeV glasses showed a decrease in quadrupole splitting (Δ) with the increase of Na_2O content, indicating a decrease in the distortion of the iron polyhedral. ^{119}Sn Mössbauer spectra of xSnV glass-ceramics nanocomposite showed an increase in Δ with the increase of Na_2O content, referring to that the structure transforms from tetrahedral to octahedral Sn^{4+}. Electrical conductivity for xFeV and xSnV before heat treatment decreased from $2.82 \cdot 10^{-5}$ to $6.61 \cdot 10^{-7}$ S cm^{-1} and 1.26 • 10^{-5} to 4.27•10^{-7} S cm^{-1} with increasing Na_2O content from 5 to 45 mol%, respectively. While 5FeV had higher electrical conductivity than any other prepared samples. According to the data obtained from charge and discharge capacity, it is concluded that 5FeV (BHT) and 5SnV (BHT) glasses can be considered good candidates for use as a cathode material for SIBs because of the large capacity of 142 and 162 mAh g^{-1} recorded after 30 cycles.

References

[1] H. Zhang, X. Liu, H. Li, I. Hasa and S. Passerini, Angew. Chem., Int. Ed., 2021, 60, 598-616.

[2] Y.Slimani, E. Hannachi, Chapter Thirteen-Nanomaterials and nanotechnology for high-performance rechargeable battery, (2021) 343-363.

[3] N. K. Rawat, I. Stoica, A. K. Haghi, Green Polymer Chemistry and Composites, (2021) 335-354.

[4] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Research development on sodium-ion batteries, Chem. Rev., 114(23) (2014) 11636-11682.

[5] R. S. Carmichael, Practical Handbook of Physical Properties of Rocks and Minerals; CRC Press: Boca Raton, FL (1989).

[6] Y. Liu, Z. Sun, K. Tan, D.K. Denis, J. Sun, L. Liang, L. Hou, C. Yuam, Recent progress in flexible non-lithium based rechargeable batteries, Mater. Chem. A, 7 (2019) 4353-4382.

[7] M.E.A. Dompablo, A. Ponrouch, P. Johansson, M.R. Palacin, Achievements, Challenges, and Prospects of Calcium Batteries, Chem. Rev., 120 (2019) 6331-6357.

[8] K.S. Kim, S. Lee, T.O. Ting, X.S. Yang, Atomic Scheduling of Appliance Energy Consumption in Residential Smart Grids, Energies, 12 (2019) 19.

[9] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, Prototype systems for rechargeable magnesium batteries, Nature, 407 (2000) 13-16.

[10] T. Jin, H. Li, K. Zhu, P.F. Wang, P. Liu, L. Jiao, Polyanion-type cathode materials for sodium-ion batteries, Chem. Soc. Rev., 49 (2020) 2342-2377.

[11] N. Yabuuchi, K. Kubota, M. Dahbi and S. Komaba, Research development on Sodium-Ion Batteries, Chem. Rev., 114 (2014) 11636-11682.

[12] P. Hejda, J. Holubová, Z. Černošek, E. Černošková, The structure and properties of vanadium zinc phosphate glasses, J. Non-Cryst. Solids, 462 (2017) 65-71.

[13] M. S. Sadeq, A. Ibrahim, The path towards wide-bandgap and UV-transparent lithium phosphate glasses doped with cobalt oxide for optical applications, J. Non-Cryst. Solids, 569 (2021) 120983.

[14] R.K. Brow, Review: the structure of simple phosphate glasses, J. Non-Cryst. Solids, 263&264 (2000) 1-28.

[15] A. Ibrahim, M.S. Sadeq, Influence of cobalt oxide on the structure, optical transitions and ligand field parameters of lithium phosphate glasses, Ceram. Int., 47 (2021) 28536-28542.

[16] G.D. Khattak, A. Mekki, L.E. Wenger, X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility studies of vanadium phosphate glasses, J. Non-Cryst. Solids, 355 (2009) 2148-2155.

[17] A. Ibrahim, M.A. Farage, M. S. Sadeq, towards highly transparent tungsten zinc sodium borate glasses for radiation shielding purposes, Ceram. Int., 48(2022) 12079-12090.

[18] N. Vedeanu, O. Cozar, I. Ardelean, B. Lendl, D.A. Magdas, U. Hoppe, N.P. Wyckoff, M.L. Schmitt, R.K. Brow, A. Schöps, A.C. Hannon, Structure of V_2O_5-P_2O_5 glasses by X-ray and neutron diffraction, J. Non-Cryst. Solids, 358 (2012) 328-336.

[19] H. Horie, Lithium-ion battery; Baifu-kan, Tokyo (2010).

[20] Y. Cai, J. Zhou, G. Fang, G. Cai, A. Pan, S. Liang, $Na_{0.282}V_2O_5$: A high-performance cathode material for rechargeable lithium batteries and sodium batteries, J. Power Sources, 328 (2016) 241-249.

[21] P. S. Kumar, S. Ayyasamy, E. S. Tok, S. Adams, M. V. Reddy, Impact of Electrical Conductivity on the Electrochemical Performances of Layered Structure Lithium Trivanadate (LiV_3-xM_xO_8, M= Zn/Co/Fe/Sn/Ti/Zr/Nb/Mo, x = 0.01-0.1) as Cathode Materials for Energy Storage, ACS Omega, 3 (2018) 3036-3044.

[22] R. Renuga, A. Manikandan, J. Arul Mary, A. Muthukrishnaraj, Anish Khan, S. Srinivasan, B. Abdullah, M. Al Alwan, K. M. Khedher, Enhanced Magneto-Optical, Morphological, and Photocatalytic Properties of Nickel-Substituted SnO_2 Nanoparticles, J.Supercond.Nov. Magn., 34 (2021) 825-836.

[23] E. Hannachi, M.I. Sayyed, B. Albarzan, A. H. Almuqrin, K.A. Mahmoud, Synthesis and study of structural, optical and radiation-protective peculiarities of $MTiO_3$ (M = Ba, Sr) metal titanate ceramics mixed with SnO_2 oxide, Ceram. Int., 47 (2021) 28528-28535.

[24] M.I.Sayyed, A. Ibrahim M.A.Abdod, M.S. Sadeq, The combination of high optical transparency and radiation shielding effectiveness of zinc sodium borate glasses by tungsten oxide additions, J. Alloys Compd., 904 (2022) 164037.

[25] E. Hannachi, M. I. Sayyed, K. A. Mahmoud, Y. Slimani, S. Akhtar, B. Albarzan, Aljawhara H. Almuqrin, Impact of tin oxide on the structural features and radiation shielding response of some ABO_3 perovskites ceramics (A = Ca, Sr, Ba; B = Ti), Appl. Phys. A, 127, 970 (2021) 1-12.

[26] M. K. Hossain, G. A. Raihan, M. A. Akbar, M.H.K. Rubel, M. H. Ahmed, M, I. Khan, S. Hossain, S. K. Sen, M. I. Jalal, A. El-Denglawey, Current Applications and Future Potential of Rare Earth Oxides in Sustainable Nuclear, Radiation, and Energy Devices: A Review, ACS Appl. Electron. Mater. 4,7 (2022) 3327-3353.

[27] M. K. Hossain, M. H. Ahmed, M, I. Khan, M. S. Miah, S. Hossain, Recent Progress of Rare Earth Oxides for Sensor, Detector, and Electronic Device Applications: A Review, ACS Appl. Electron. Mater. 3, 10, (2022) 4255-4283.

[28] N. Ghaedsharafia, G. Shamsa, Z. Soltani, Phase Formation and Conductivity Fluctuation Investigation in Nanoparticle SnO_2-Added $Y_3Ba_5Cu_8O_{18\pm\delta}$ Polycrystalline Superconductor, Phy. Solid State, 62 (2020) 2154-2166.

[29] S. Kubuki, H. Masuda, K. Matsuda, K. Akiyama, A. Kitajou, S. Okada, P. Zsabka, Z. Homonnay, E. Kuzmann, T. Nishida, Mössbauer study of new vanadate glass with large charge-discharge capacity, Hyperfine Interact., 226 (2014) 765-770.

[30] S. Kubuki, H. Masuda, K. Matsuda, K. Akiyama, Z. Homonnay, E. Kuzmann, T. Nishida, Electrical conductivity and local structure of lithium tin iron vanadate glass, Hyperfine Interact, 219 (2013) 141-145.

[31] S. Kubuki, K. Osouda, A.S. Ali, I. Khan, B. Zhang, A. Kitajou, S. Okada, J. Okabayashi, Z. Homonnay, E. Kuzmann, T. Nishida, L. Pavic´, A. Santic´, A.M Milankovic´, ^{57}Fe - Mössbauer and XAFS studies of conductive sodium Phosphor-Vanadate glasses as a cathode active material for Na-ion batteries with large capacity, J. Non-Cryst. Solids 570 (2021) 120998-121010.

[32] L. Yang, Y. Lei, X. Liang, L.Qu, K. Xu, Y. Hua, J. Feng, SnO_2 nanoparticles composited with biomass N-doped carbon microspheres as low cost, environmentally friendly and high-

performance anode material for sodium-ion and lithium-ion batteries, J.Power Sources, 547 (2022) 232032.

[33] M.Y. Hassaan, M.G. Moustafa, K. Osouda, S. Kubuki, T. Nishida, ^{57}Fe and ^{119}Sn Mössbauer, XRD, FTIR and DC conductivity study of Li_2O - Fe_2O_3-SnO_2 -P_2O_5 glass and glass-ceramics J. Alloys Compd.,765 (2018) 121-127.

[34] T. Nishida, M. Suzuki, S. Kubuki, M. Katada, Occupation of tungsten site by iron in sodium tungstate glasses, J. Non-Cryst. Solids, 194 (1996) 23-33.

[35] M. Farouk, A. Samir, A. Ibrahim, M. A. Farag, A. Solieman, Raman, FTIR studies and optical absorption of zinc borate glasses containing WO_3, J. Appl. Phys. A, 126 (2020) 1-8.

[36]M. A. Farag, A. Ibrahim, M. Y. Hassaan, R. M. Ramadan, Enhancement of structural and optical properties of transparent sodium zinc phosphate glass-ceramics nanocomposite, J. Aust. Ceram. Soc., 58 (2022) 653-661.

[37] J. S. J. Hargreaves, Some considerations related to the use of the Scherrer equation in powder X-ray diffraction as applied to heterogeneous catalysts, Catalysis, Structure & Reactivity, 2 (2016) 33-37.

[38] M.S. Park, G. X. Wang, Y.M. Kang, D. Wexler, S.X. Dou, H.K. Liu, preparation and electrochemical properties of SnO_2 nanowires for application in lithium-ion batteries, Angew. Chem. 46(2007)750-753.

[39] T. Nishida, Advances in the Mössbauer effect for the structural study of glasses, J. Non-Cryst. Solids, 177 (1994) 257-268.

[40] I. Furumoto, S. Kubuki, T. Nishida, Mössbauer study of water-resistive conductive vanadate glass, J. Radioisotopes, 61(2012) 463- 468.

[41] K. Matsuda, S. Kubuki, K. Akiyama, Z. Homonnay, K. Sinko, E. Kuzmann, T. Nishai, A relationship between electrical conductivity and structural relaxation of $10SnO_2$. $10Fe_2O_3$.xAgI.(70-x)V_2O_5 glass caused by heat-treatment, J. Ceram. Soc. Japan, 123(2015) 121-128.

[42] H. Aboud, R. J. Amjad, SnO_2 nanoparticles concentration-dependent structural and luminescence characteristics of Er^{3+} doped zinc-lead phosphate glass, J. Non-Cryst. Solids 471 (2017) 1-5.

[43] L. Pavi, A. Santi, J. Nikolic, P. Mosner, L. Koudelka, D. Pajic, A. Mogus-Milankovi, Nature of mixed electrical transport in Ag_2O-ZnO-P_2O_5 glasses containing WO_3 and MoO_3, Electrochim. Acta, 276 (2018) 434-445.

[44] A. Šantić, J. Nikolić, S. Renka, L. Pavić, Petr Mošner, L. Koudelka, Grégory Tricot, Andrea Moguš-Milanković, A versatile role of WO_3 and MoO_3 in electrical transport in phosphate glasses, Solid State Ionics, 375 (2022) 115849.

[45] Ģ. Vītiņš, Z. Kaņepe, A. Vītiņš, J. Ronis, A. Dindūne, A. Lūsis, Structural and conductivity studies in $LiFeP_2O_7$, $LiScP_2O_7$, and $NaScP_2O_7$, J. Solid State Electro. chem., 4 (3) (2000) 146-152.

[46]A. Langrock, Y. Xu, Y. Liu, S. Ehrman, A. Manivannan, C.Wang, Carbon coated hollow Na_2FePO_4F spheres for Na- ion battery cathodes, J. Power Sources, 223, (2013) 62-67.

[47] T. Nisida, Y. Fujita, S. Shiba, S. Masuda, N. Yamaguchi, T. Izumi, S. Kubuki, N. Oka, ^{119}Sn and ^{57}Fe Mössbauer study of highly conductive vanadate glass, J. Mater. of Science A 216 (2019)8847-8854.

[48] M. G. Moustafa, Electrical transport properties and conduction mechanisms of semiconducting iron bismuth glasses, Ceram. Int., 42 (2016) 17723-17730.

[49] S. Mukherjee, N. Schuppert, A. Bates , J. Jasinski ,J. Hong, M. Choi, S. Park, An electrochemical and structural study of highly uniform tin oxide nanowires fabricated by a novel, scalable sold plasma technique as anode material for sodium-ion batteries, J. Power Sources, 347 (2017) 201-209.

[50] Y. Cao, X. Xia, Y. Lia, N. Wang, J. Zhang, D. Zhao, Y. Xia, Scalable synthesizing nano-spherical $Na_4Fe_3(PO4)_2(P_2O_7)$ growing on MCNTs as a high-performance cathode material for sodium-ion batteries, J. Power Sources 461, (2020)228130.

[51] Y. Cao, Y. Liu, D. Zhao, J. Zhang, X. Xia, T. Chen, L. Zhang, P. Qin, Y. Xia, K- doped $Na_3Fe_2(PO_4)_3$ cathode materials with high-stable structure for sodium-ion stored energy battery, J. Alloys compd.,784 (2019) 939-946.

[52] S. Bach, N. Baffier, J.P. Pereira-Ramos, R. Messina, Electrochemical sodium intercalation in $Na_{0.33}V_2O_5$ bronze synthesizes by a sol-gel process, Solid-state Ionics, 37 (1989) 41- 49.

[53] Y. Dong, J. Xu, M. Chen, Y. Guo, G. Zhou, N. Li, S. Zhou, C. P. Wong, Self-assembled NaV_6O_{15} flower-like microstructure for high-capacity and long-life sodium-ion battery cathode, J. Nano Energy 68 (2020) 104357-104367.

[54] S. Yuan, Y.B. Liu, D. Xu, D.L. Ma, S. Wang, X.H. Yang, Z.Y. Cao, X.B. Zhang, Pure Single-Crystalline $Na_{1.1}V_3O_{7.9}$ nanobelts as superior cathode materials for rechargeable sodium-ion batteries, Adv. Sci., 2 (2015) 1400018-1400024.

[55] Y.F. Dong, S. Li, K.N. Zhao, C.H. Han, W. Chen, B.L. Wang, L. Wang, B.A. Xu, Q. L. Wei, L. Zhang, X. Xu, L.Q. Mai, Hierarchical zigzag $Na_{1.25}V_3O_8$ nanowires with topotactically encoded superior performance for sodium-ion battery cathodes, Energy Environ. Sci. 8 (2015) 1267-1275.

[56] Y. Cai, J. Zhou, G. Fang, A. Pan, S. Liang, $Na_{0.282}V_2O_5$: A high-performance cathode material for rechargeable lithium batteries and sodium batteries, J. Power Sources 328 (2016) 241–249.

[57] S. Hartung, N. Bucher, J.B. Franklin, A. Wise, L.Y. Lim, H. Chen, J. Nelson, M.E. Weker, M.F. Toney, M. Srinivasan, Mechanism of Na^+ insertion in alkali vanadates and its influence on battery performance, Adv. Energy Mater. 6 (2016) 1502336 -1502347.