Crystallization of the Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ Glass and Ability of Cathode for Sodium-Ion Batteries

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Although the sodium phosphate cathode active materials based on the Ni$^{3+}$/Ni$^{2+}$ redox reaction are expected to develop a high discharge potential, none of the studies aimed at practical application have been reported due to its poor kinetics showed in the sodium phosphate. Herein, we substituted active Fe for a part of Ni, expecting to activate the potential deriving from the Ni$^{3+}/^{2+}$ in Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ glass-ceramics. Precursor glasses were prepared by the melt-quenching method and exhibited surface crystallization tendency due to heterogeneous nucleation. In the charge-discharge testing, all the flat potential showed in the discharge process derived from the reduction of Fe$^{3+}/^{2+}$. However, from the dQ/dV plot, there were two weak reduction peaks at 4.3 and 4.4 V in the discharge process of Na$_2$Fe$_{0.25}$Ni$_{0.75}$P$_2$O$_7$. Combining with the oxidation peak at 4.6 V in the second charge process of Na$_2$NiP$_2$O$_7$, we believe the reduction peaks at 4.3 and 4.4 V were derived from the Ni$^{3+}/^{2+}$.

Keywords: glass-ceramics, crystallization behavior, sodium-ion batteries, cathode materials, charge-discharge test

INTRODUCTION

At present, Lithium-Ion Rechargeable Batteries (LIBs) are widely applied to small electronic equipment such as mobile phones and laptop computers, due to the high voltage, high energy density, and long charge-discharge cycle life (Nishi, 2001; Nitta et al., 2015). However, high cost and low safety (Spotnitz and Franklin, 2003; Wang et al., 2012; Finegan et al., 2015) are becoming enormous challenges for them. On the other hand, accompanied by the development of science and technology, drastic improvement of the energy and power density is required, so developing new electrode materials is necessary.

Considering the abundance of sodium ions existing (Slater et al., 2013) and the nearest ion radius with lithium-ion in the group of alkali metal elements in the periodic table, quantities of researchers paid their attention to sodium rechargeable batteries. As a matter of fact, due to the dense atomic mass and larger ionic radius, SIBs commonly generate a lower energy density (Kundu et al., 2015) and a shorter cycle life (Ong et al., 2011) than LIBs. Therefore, the object of these problems is the most critical challenge for SIBs. Some researchers focus on cathode materials to promote the storage of sodium ions. There are numerous types of cathode materials for SIBs had been reported, such as transition-metal layered oxides Na$_x$MO$_2$ (Yabuuchi et al., 2012; Wang et al., 2016), Phosphates NaMPO$_4$ (Fang et al., 2015; Bianchini et al., 2018), Pyrophosphates Na$_2$MP$_2$O$_7$ (Honma et al., 2012, 2013; Barpanda et al., 2013b), Fluorophosphates Na$_2$MPO$_4$F...
Sulfates Na$_2$M$_2$(SO$_4$)$_3$ (Barpanda et al., 2014) and NaM(SO$_4$)$_2$ (Singh et al., 2015). In addition to exploiting the cathode materials, synthesis should be low-cost. Crystallization of glasses is a simple method, which starting from the low-cost precursor glasses for the fabrication of crystalline materials with desired shapes and functions (Komatsu, 2015; Deubener et al., 2018). Glass-forming oxide P$_2$O$_5$ makes this an excellent method to synthesis Phosphates and Pyrophosphates. 

However, in the Na$_2$FeP$_2$O$_7$ compound with a little Fe substitution, it appeared a high potential of 3.8 V derived from Mn$^{4+}$ ions (Chung et al., 2002). This compound has a high electrical performance of some active materials in LIBs or SIBs (Tsukuda et al., 2013). Therefore, the appearance of NiP$_2$O$_7$ was reported that Ni was not active in the pyrophosphate framework under the electric test (Chung et al., 2002). 

Furthermore, a similar result was also obtained in Na$_2$MnP$_2$O$_7$ glass-ceramics with non activity of Mn$^{2+}$ (Tanabe et al., 2018). However, in the Na$_2$Fe$_{0.25}$Mn$_{0.75}$P$_2$O$_7$ compound with a little Fe substitution, it appeared a high potential of 3.8 V derived from Mn$^{3+}$/$^{2+}$ (Tanabe et al., 2018). Therefore, the appearance of Ni$^{3+}$/$^{2+}$ in higher potential with Fe substitution is expected. In this study, the crystallization behavior, density, and electrochemical properties of Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ glass or glass-ceramics will be reported for the first time.

**EXPERIMENTS**

The precursor Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ glasses ($x = 1, 0.75, 0.5, 0.25, 0$) were prepared by melt-quenching method. Under the composition of 33.3Na$_2$O-33.3xFeO-33.3 (1–x) NiO-33.3P$_2$O$_5$ (mol%), the precursor chemicals sodium dihydrogen phosphate (98.0% Na$_2$HPO$_4$, Nakarai Tesque Co., Japan), iron mono-oxide (99.5% FeO, Kojundo Chemicals Co., Japan) and nickel mono-oxide (99.9% NiO, Kojundo Chemicals Co., Japan) were weighted and mixed. Then the mixed Na$_2$NiP$_2$O$_7$ powder was melted in a platinum crucible at 1,200°C for 30 min in the nitrogen atmosphere, and other composition powder was melted in a graphite crucible at 1,200°C for 30 min in the nitrogen atmosphere by an electric furnace. The melt was then poured onto a steel plate and quenched with another steel plate to produce a bulk glass precursor.

In order to confirm the amorphous state and identify the crystalline phase, the X-ray diffraction (XRD) was performed on Rigaku Ultima IV X-ray diffractometer (Rigaku, Japan) equipped with Cu-Ka radiation (40 kV, 40 mA, and $\lambda = 0.154056$ nm) in a speed of 5 deg./min between 10 and 70 deg. The density of the samples was determined by using the XS205 Dual Range analytical balance (METTLER TOLEDO, Germany) by the Archimedes principle. Differential thermal analysis (DTA, Thermoplus EVO TG-8120, RIGAKU Corp., Japan) was used to determine the glass transition temperature $T_g$, glass crystallization onset temperature ($T_c$), and glass crystallization temperature $T_p$ of the samples. All the processes performed under the N$_2$ atmosphere, and the temperature scanning rate of 10 K min$^{-1}$. Scanning Electron Microscope (SEM, KEYENCE VE-8800) was used to check the crystallization behavior of the glasses.

Because of the strong covalent bond in the pyrophosphates could lead to a low electric conductivity, so the carbon coating was necessary (Chung et al., 2002). An automatic mortar ground the glass precursors for 30 min and selected by a sieve in which the particle size was under or equalled 105 µm. And then, the mixture composed of glass precursors and carbon black (CB) in a weight ratio of 84.2: 15.8 placed into a ZrO$_2$ pot (45 cm$^3$) together with 50 g balls (3 mm) and 10 ml methanol, so the mixture would be mixed and pulverized for 15 min $\times$ 4 cycles in 700 rpm by wet ball-milling (FRITSCH Premium line P7). After wet ball-milling, we used an evaporator (Tokyo Rika Kikai, N-1110V) to distill off the rudimental methanol and dried the mixture (glass/CB)
at 80°C for 1 h. In order to fabricate the positive electrode materials, we did a heat-treatment regarding the mixture of Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ glass and CB. Heat-treatment was performed on glass crystallization temperature $T_p$ for 3 h under a nitrogen atmosphere. We used Polyvinylidene fluoride (PVDF) as a binder with the mixture of crystallized Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ glass-ceramics and graphite in a weight ratio 5:95 in a mortar. In order to prepare a slurry to coat on the aluminum foil, we dropped a little N-methylpyrrolidone (NMP) as a solvent to mix with that and dried the coated Al foil at 80°C for 1 h. Finally, the positive electrode was punched out as 16 mmφ and dried at 100°C in a vacuum oven all night. Sodium metal foils were used as the negative electrodes, the glass filter papers (Advantec Co., GA-100) were used as a separator, and the solution of 1 M NaPF$_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v) was used as the electrolyte. The test cells were assembled by the flat cells in an argon-filled glove box, in which the dew point temperature kept at −86°C. The charge-discharge test was performed at a cutoff voltage of 1.5–4.9 V and a rate of 1/10 C by a battery testing system (Hokuto-denko Co.).

The theoretical capacity and corresponding electrochemical reaction formula is showing below:

$$\text{Theoretical capacity (mAh/g)} = \frac{n \, (\text{mol}) \times F \, (\text{C/mol})}{M \, (\text{g/mol}) \times 3600 \, (\text{s/h}) \times 1000 \, (\text{mA/A})}$$

$n$ is the theoretical mole number of the de-insertion sodium ions; $F$ is the Faraday constant; $M$ is the mole mass of the cathode material.

The electrical resistance of glass-ceramics was measured in the form of a pellet with a thickness of 1.0 mm by an alternating current (AC) impedance method (HIOKI 3522-50 LCR Hi-TESTER, Japan) with the electrode diameter of 6.0 mmφ in the frequency range of 4–100 kHz.

**RESULTS AND DISCUSSION**

**Amorphous State**

**Figure 1** shows the appearance of the fabricated precursor glasses. Na$_2$NiP$_2$O$_7$ showed a rust-red color and high density of the fabricated Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ glass and Na$_2$MnP$_2$O$_7$ (M = Ni, Fe) crystal.  

**Figure 2** | XRD patterns of the fabricated Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$: (A) bulk; (B) powder.
transparency. However, the other samples showed a black color, and only the Na$_2$Fe$_{0.25}$Ni$_{0.75}$P$_2$O$_7$ exhibited low transparency. XRD patterns of the bulk and powder, which was pulverized from bulk by an agate mortar of the obtained samples, are shown in Figure 2. All samples showed the typical halo patterns of amorphous with no crystallization.

**Density Measurement**

Figure 3 shows the density result of the fabricated glasses. So we can see that as the x (FeO content) increasing, the density of the glasses tends to be decreasing as a straight line, owing to the molecular weight of FeO is smaller than that of NiO. Figure 3 also shows the calculated theoretical density of the Na$_3$MP$_2$O$_7$ ($M$ = Ni, Fe) crystal in Figure 3. So we can see that the density of Na$_2$NiP$_2$O$_7$ glass is about 97.9% of Na$_2$NiP$_2$O$_7$ crystal, and the density of Na$_2$FeP$_2$O$_7$ glass is about 95.2% of Na$_2$FeP$_2$O$_7$ crystal. The two unparallel lines of the glass and crystal densities changes indicated that there was a little part of oxidized Fe$^{3+}$ existed in the glass. Because Fe$^{3+}$ ions are more natural to form tetrahedral configuration, so the real density of Na$_2$FeP$_2$O$_7$ glass is smaller than the theoretical value with all Fe$^{2+}$ hexahedral configuration. By the way, for the existing of Fe$^{3+}$, the glasses were fabricated easier, and the network of the glasses will be more stable. Such behavior can be confirmed in the process of glass fabrication (Hirose et al., 2008; Honma et al., 2010).

**Crystallization Mechanism**

Figure 4 shows the DTA curves of bulk and powder of the obtained samples. The endothermic dips suggest the glass transition temperature ($T_g$), and the exothermic peaks suggest the glass crystallization temperature ($T_p$). The crystallization onset temperature ($T_x$) is also shown in Figure 4. However, we can see that there is a considerable crystallization behavior difference between bulk and powder of Na$_2$FeP$_2$O$_7$ from the DTA results. Because the shape of the DTA pattern is sensitive to the oxidized surface area of the bulk and powder, the $T_g$ and $T_x$ of the glass powder are much higher than those of the bulk glass.

The heat-treatment temperature was depended on the glass crystallization temperature ($T_p$) of the powder, so the heat-treatment was performed on 544, 548, 564, 589, and 610°C. The XRD patterns of that are shown in Figure 5. Na$_{3.12}$Fe$_{2.44}$(P$_2$O$_7$)$_2$ (Angenault et al., 1995) crystal was obtained from the Na$_2$FeP$_2$O$_7$ and Na$_{3.14}$Ni$_{2.18}$(P$_2$O$_7$)$_2$ crystal (Erragh et al., 2000) was obtained.
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FIGURE 6 | XRD pattern and Rietveld refinement for the mixture of heat-treated Na$_2$NiP$_2$O$_7$ and CB.

FIGURE 7 | Crystal structure of Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$, (A) Ni-Fe substitution type 1; (B) Ni-Fe substitution type 2. Na (yellow), Fe (blue), Ni (green), P (purple), O (red).

from the other composition of Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ ($x = 0.75$, 0.5, 0.25, and 0). The simulated patterns of the two kinds of crystals are also shown in Figure 5, which with no other crystal phase precipitated.

In order to analyze the Na$_2$NiP$_2$O$_7$ crystalline phase in the mixture of Na$_2$NiP$_2$O$_7$ glass-ceramics and CB, Rietveld refinement on the powder XRD pattern was performed, and the result is shown in Figure 6. According to the Na$_{3.14}$Ni$_{2.18}$(P$_2$O$_7$)$_2$ crystal structure, which is shown in Figure 7, the group of PO$_4$(tetrahedral), NiO$_6$(octahedral), and FeO$_6$(octahedral) units combine by corner-sharing to provide a stable three-dimensional framework to support the de-insertion along the (100) direction of sodium ions. Two types of Ni-Fe substitution were discussed, basing on the position of the Ni atoms. The image of type 1 is shown in Figure 7A, which suggests that the Ni-Fe substitution occurred in the NiO$_6$ units. Besides, the image of type 2 is shown in Figure 7B. It suggests that Fe substituted a part of Ni in the Na (1) sites, which contained about 80% Na and 20% Ni. Owing to the two kinds of substitution type could not be decided which one was main, so lattice parameters were analyzed out by Rietveld refinement.

We summarized the lattice parameters of the crystalline phase as shown in Table 1. It also shows clearly in Figure 8 that with the Fe substitution increasing, $a$, $b$, $c$ axes, and volume were going up at the same time. However, alpha, beta, gamma did not exhibit any component dependency. Because the ionic radius of Fe$^{2+}$ is larger than that of Ni$^{2+}$, so the Ni-Fe substitution existed in the Na$_2$NiP$_2$O$_7$ crystal. Since the Ni-Fe substitution type 1 has a significant influence on the crystal structure, it could be the primary way of Ni-Fe substitution. When the lattice parameters ($a$, $b$, $c$) increased by Ni-Fe substitution, the crystal volume got larger than before, and it will be advantaged for the de-insertion of sodium ions.

We did the heat-treatment between $T_g$ and $T_x$ on the Na$_2$FeP$_2$O$_7$ and Na$_2$NiP$_2$O$_7$ bulk glasses and observed the crystallization behavior by SEM. Figure 9 shows the SEM images of a fracture surface of the samples crystallized by heat.
The same crystallization behavior can be observed that both Na$_2$FeP$_2$O$_7$ and Na$_2$NiP$_2$O$_7$ bulk glasses prefer to develop the crystalline phase on the glass surface. Surface crystallization can lead to high crystal orientation, so such outstanding crystallization behavior is expected to improve the ionic conduction of cathode materials (Akatsuka et al., 2018). Another aspect, the Na$_2$NiP$_2$O$_7$ glass exhibits thermal instability because the $\Delta T$ ($T_{\text{heat-treatment}} - T_g$) is only 8°C. Hence, we obtained more thick surface crystallized architecture in Na$_2$NiP$_2$O$_7$ rather than Na$_2$FeP$_2$O$_7$.
Electrochemical Properties

The result of the first and second charge-discharge curves of the Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ glass-ceramics is shown in Figure 10A. The initial discharge capacity of Na$_2$Fe$_x$Ni$_{1-x}$P$_2$O$_7$ from $x = 0$ to $0.75$ were 14.6, 21.8, 31.4, and 57.6 mAh/g. Each one was lower than that of Na$_2$FeP$_2$O$_7$ (68.7 mAh/g). It indicated that with the Fe
content increasing, the discharge capacity would be going up. In other words, it will be active with the Fe substitution increasing. Furthermore, all the flat potential 3.0 or 2.5 V exhibited in the discharge process derived from the reduction of Fe$^{3+/2+}$ (Honma et al., 2012). However, the flat potential of Ni$^{3+/2+}$ did not exhibit in any composition. Even in the discharge process of Na$_2$Fe$_{0.25}$Ni$_{0.75}$P$_2$O$_7$, there was only a 2.0 V flat potential of Fe$^{3+/2+}$, suggesting the overvoltage caused by the inactive Ni.

To check the redox peaks in the process of charge and discharge, dQ/dV plots that transformed from the charge-discharge curves are shown in Figure 10B. In the 1st charge-discharge process of Na$_2$NiP$_2$O$_7$, there was no redox peak exhibited out, which showed the same result with Zhang et al. (2017). However, in the 2nd charge process, there was an oxidation peak of Ni$^{2+/3+}$ at about 4.6 V (Zhang et al., 2017) exhibited. In addition, in the discharge process of Na$_2$Fe$_{0.25}$Ni$_{0.75}$P$_2$O$_7$, despite there could be a weak electrolytic solution decomposition potential at about 4.3 V, it still exhibited the potential of Ni$^{3+/2+}$ at about 4.3 and 4.4 V. As a result, Na$_2$Fe$_{x}$Ni$_{1-x}$P$_2$O$_7$ with the Fe substitution up to $x = 0.25$ will activate the Ni$^{3+/2+}$. However, in total, Ni$^{3+/2+}$ in the composition of Na$_2$Fe$_{0.25}$Ni$_{1-x}$P$_2$O$_7$ exhibited inactivity.

To know the electrical conductivity of the positive electrode materials, we decided to measure their electrical resistance from 100 to 220°C. Considering the difference of crystallization behavior between bulk and powder, we chose to press the precursor glass powder as a pellet and then measured the electrical resistance of the pellets after heat-treatment under $T_p$. Figure 11 shows Nyquist plots of crystallized Na$_2$Fe$_{x}$Ni$_{1-x}$P$_2$O$_7$ pellets. The intersection of semicircle and horizontal axis determined the electrical resistance, so with the Fe substitution increased, the electrical resistance would be decreased. In other words, electrical conductivity would be increased. However, there was a result that the electrical resistance of Na$_2$Fe$_{0.25}$Ni$_{0.75}$P$_2$O$_7$ pellet was higher than that of the other components, which could confirm the same result exhibited in charge-discharge curves. Because of the exceptional electrical resistance exhibited in the composition of Na$_2$Fe$_{0.25}$Ni$_{0.75}$P$_2$O$_7$, so the reduction of Fe$^{3+/2+}$ would be alleviated. With the alleviating of Fe$^{3+/2+}$, the reduction peaks of Ni$^{3+/2+}$ which could be activated by the substituted Fe$^{2+}$ exhibited out. However, the reduction peaks of Ni$^{3+/2+}$ disappeared at the composition $x = 0.5$ and 0.75. It may be owing to the active Fe$^{3+/2+}$ reduction reaction is dominant so the Ni$^{3+/2+}$ reduction reaction will be unavailable.

No matter which kind type of Ni-Fe substitution, it will influence the electric conductivity (Sanz et al., 2001) so that the Ni$^{2+}$ which surrounds the substituted Fe$^{2+}$ will be activated. Also, carbon-coatings will enhance the electrochemical behavior of the materials contained Fe (Wang and Sun, 2012), which can ensure a better charge-discharge cycle. However, the liquid electrolyte 1 mol/L EC: DEC [1:1 (vol%)]-NaPF$_6$ showed a decomposition potential at about 4.3 V. It could influence Ni$^{3+/2+}$ redox so that Ni$^{3+/2+}$ which has the higher potential (Zhang et al., 2017) did not exhibit out before 4.9 V. Because of the limitation of the liquid electrolyte, seeking the electrolyte with high decomposition potential is necessary.

CONCLUSION

In conclusion, the Na$_2$Fe$_{x}$Ni$_{1-x}$P$_2$O$_7$ glasses were prepared by the melt-quenching method successfully. Moreover, the precursor Na$_2$Fe$_{x}$Ni$_{1-x}$P$_2$O$_7$ glasses were confirmed that they contained a part of Fe$^{2+}$, which was oxidized from Fe$^{2+}$. Na$_3$Ni$_{12.18}$(P$_2$O$_7$)$_2$ crystal which was obtained from heat-treated Na$_2$Fe$_{x}$Ni$_{1-x}$P$_2$O$_7$ glass-ceramics, mainly with type 1 Ni-Fe substitution. With the Fe substitution increasing in the Na$_3$Ni$_{12.18}$(P$_2$O$_7$)$_2$ crystal, it performed a higher activity. In the composition of Na$_2$Fe$_{x}$Ni$_{0.75}$P$_2$O$_7$, the reduction peaks of 4.3 and 4.4 V appeared in the discharge process. Although reversible charge-discharge reaction could not confirm due to interference with electrolyte oxidation, application to oxide all-solid-state batteries is expected to expand to batteries with higher energy density than sodium iron phosphate derived all-solid batteries.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation, to any qualified researcher.

AUTHOR CONTRIBUTIONS

YJ demonstrated all experiments in the study. TH proposed glass-ceramic cathode for sodium ion battery. TK proposed the preparation of glass-ceramics and the analysis of surface crystallization.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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