# Fabrication of Na₂FeP₂O₇ glass-ceramics for sodium ion battery

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New cathode candidate $Na_2FeP_2O_7$ for rechargeable sodium ion second battery was successfully prepared by glass-ceramics method. The precursor glass, which is same composition in $Na_2FeP_2O_7$, was prepared by melt-quenching method. $Na_2FeP_2O_7$ was obtained by heat treatment of precursor glass powder with 10% glucose addition as reduction agent of $Fe^{3+}$ at 620°C for 3 h in electric furnace. $Na_2FeP_2O_7$ has triclinic P1-structure with $a = 0.64061$ nm, $b = 0.938893$ nm, $c = 1.09716$ nm, $\alpha = 64.5381°$, $\beta = 86.0580°$, $\gamma = 73.0619°$. By means of electrochemical charge–discharge testing, $Na_2FeP_2O_7$ exhibits 2.9 V, 88 mAh/g, in which is 90% for the theoretical capacity during 2.0–3.8 V cut-off voltages. $Na_2FeP_2O_7$ ceramics has the potential for the safety cathode candidate for the sodium ion battery with a low materials cost.
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## 1. Introduction

Recently, poly-anion based $LiFePO_4$ has been much attracted for the next generation lithium ion second battery.[1] $LiFePO_4$ has superior thermal and electrochemical stability compared with conventional $LiCoO_2$, $LiMn_2O_4$ cathode materials. On the other hand the other alkaline and alkaline earth ion based second batteries are proposed. In especially sodium ion is being just under the lithium in periodic table and exhibits higher voltage (2.7 V for $Na/Na^+$) after lithium ion (3.03 V for $Li/Li^+$).

Layered rock salt structured $NaCrO_2$, which is same as $LiCoO_2$, is known as cathode active materials for sodium ion battery.[2] Although $NaCrO_2$ exhibits good electronic conductivity and sodium ion intercalation, but the lacking of electrochemical stability prohibits its utilization. Phosphate based $NaFePO_4$, which is same composition in $LiFePO_4$, is not suitable for the cathode materials because of complex poly anion units disturb sodium ion conduction.[3] Therefore there are only a few cathode candidates for sodium ion battery. Development of new cathode active materials is needed for the realization of sodium ion battery.

We are proposing unique technique to fabricate phosphate based cathode materials such as olivine structured $LiFePO_4$ and NASICON structured $Li_3V_2(PO_4)_3$ ceramics by crystallization process from glass precursor.[4]–[7] Precursor glass has very homogeneous compositional distribution hence we obtained any ferromagnetic byproduct free $LiFePO_4$ which working even in high-speed charge–discharge condition.[7]

In this study we found new cathode candidate $Na_2FeP_2O_7$ triclinic $\bar{P}_1$ crystal that fabricated by glass-ceramics process. We examined its crystallization behavior and electro-chemical properties.

## 2. Experimental

The $Na_2FeP_2O_7$ precursor glass was fabricated by conventional melt-quenching method. Starting reagent $NaPO_3$ (Nakarai tesque) and $Fe_2O_3$ (Kojyundo chemicals) was mixed and melted in platinum crucible at 1200°C for 10 min in electric furnace. By

pouring melts on the steel plate the black-colored precursor glass was successfully formed. The glass transition temperature and crystallization temperature was determined by differential thermal analysis (DTA, Rigaku TG-8120). Glass powder which grain size is about 2 μm was obtained by using of planetary ball mill (Fritsch premium line P-7). Glass ceramics was prepared by heat treatment in 5%$H_2$–95%Ar gas flowed tubular electric furnace at 620°C for 3 h. To reduce $Fe^{3+}$ ion in precursor glass 10 wt% glucose was added glass powder. The amount of residual carbon content was determined by thermogravimetric analysis (TG–DTA, Rigaku TG-8120). Powder X-ray diffraction (XRD, Rigaku UltimaIV) employing Cu K$\alpha$ radiation was used to identify the crystalline phase of prepared powders. The concentration of $Fe^{2+}$ in the glass and glass-ceramics with the composition of $Na_2FeP_2O_7$ was determined using a cerium redox titration method, in which 0.1N–$Ce(SO_4)_2$/$H_2SO_4$ aqueous solution as titrant and ortho-phenanthroline as indicator were used. The cathode electrodes were fabricated from a mixture of active material, polyvinylidene fluoride (PVDF) and conductive carbon black in a weight ratio of 85:5:10. N-methylpyrolidone (NMP) was used to make the slurry of the mixture. After homegenenization, the slurry was coated on a thin aluminum foil and dried at 90°C for 10 h in a vacuum oven. The electrode was then pressed and disks were punched out as 16 mm$\phi$. The electrochemical cells were prepared using coin type cells. Sodium metal foils were used as anode, and glass filter paper (Advantec Co., GA-100) was used as separator. Test cell was assembled in an argon-filled glove box. The dew point of Ar atmosphere in glove box was kept as −86°C. The solution of 1 M $NaPF_6$ (Tokyo Kasei Co.) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v, Kishida Chemicals Co.) was used as electrolyte. The cells were examined by using a battery testing system (Hokuto-denko Co.) at current density of 1/10 (0.02 mA/cm²) for the theoretical capacity as 97 mAh/g between 2.0 and 3.8 V.

## 3. Results and discussion

The bulk DTA pattern of $Na_2FeP_2O_7$ precursor glass is shown in **Fig. 1**. The glass transition ($T_g$) was determined as 450°C and the crystallization peak was determined as 580°C respectively. Furthermore an endothermic temperature was found at 693°C

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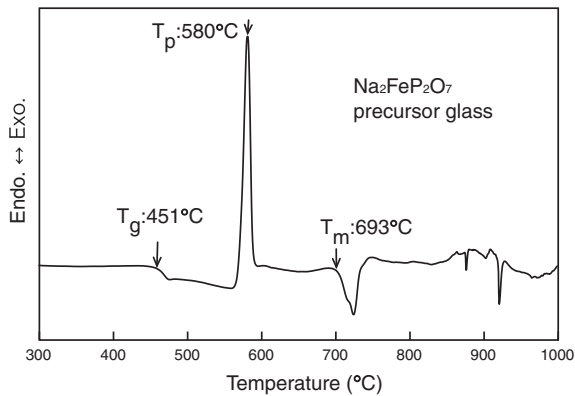† Corresponding author: T. Honma; E-mail: honma@mst.nagaokaut.ac.jp

Fig. 1.   The DTA patterns of the $Na_2FeP_2O_7$ precursor glass.



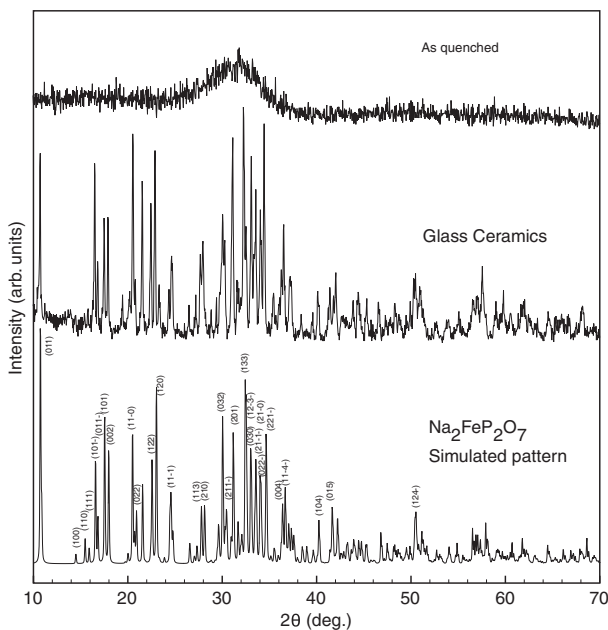Fig. 2.   The powder XRD patterns for the as quenched precursor glass, glass-ceramics and simulated patterns of $Na_2FeP_2O_7$.



Fig. 3.   (Color online) Crystal structure of triclinic $Na_2FeP_2O_7$ phase.
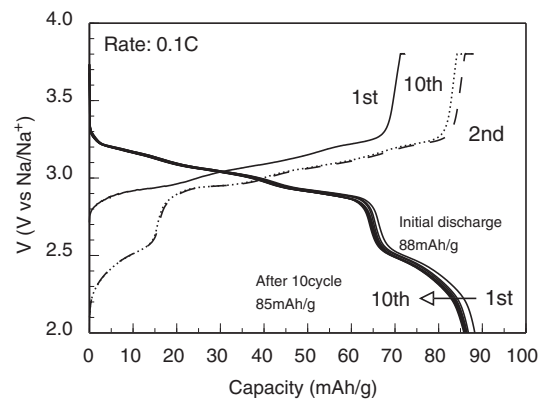


Fig. 4.   Charge–discharge curves during 10 cycles in test cell. The discharge rate was fixed as 0.1 C.

that corresponding melting point. According from the results of DTA measurement we determined heat-treatment temperature to fabricate $Na_2FeP_2O_7$ glass-ceramics as 620°C.

The powder XRD patterns for the as quenched precursor glass and glass-ceramics heat-treated at 620°C for 3 h in $H_2$–Ar gas were shown in **Fig. 2**. The percentage of residual carbon content was estimated as 1.9 wt% by means of TG–DTA analyses. It clearly seems sharp diffractions corresponding to the presence of crystalline phase. To refine the crystal structure in $Na_2FeP_2O_7$ we examined the Rietvelt analysis. We used and modified the crystal structure of triclinic $Na_{3.12}Fe_{2.44}(P_2O_7)_2$ reported by Angenault et al.[8] The determined crystal structure of $Na_2FeP_2O_7$ was illustrated in **Fig. 3** and the simulated XRD pattern is also shown in Fig. 2. All diffractions are agreed with simulated patterns. Obtained $Na_2FeP_2O_7$ has triclinic $P1$-structure. The parameters of unit cell are $a = 0.64061$ nm, $b = 0.938893$ nm, $c = 1.09716$ nm, $\alpha = 64.5381°$, $\beta = 86.0580°$, $\gamma = 73.0619°$. The presence of mainframe consisted from $P_2O_7$ and $FeO_6$ unit is a unique feature. According to crystal structure shown in Fig. 2 large tunnel structure is exist along with (100) direction to diffuse sodium ions. The precursor glass melted under air condition. According
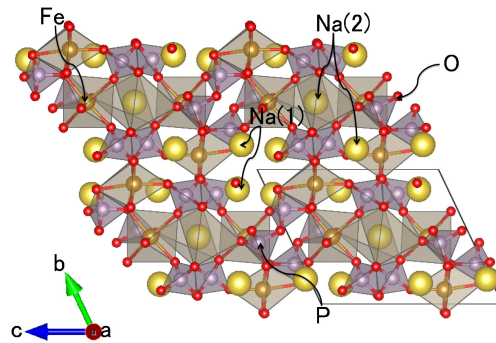
to the red-ox titration to determine valence state of iron, the precursor glass contains 9.1% $Fe^{2+}$ for the total amount of Fe and the glass-ceramics contains 96.2% $Fe^{2+}$. It is clear that valence state completely change from $Fe^{3+}$ to $Fe^{2+}$ during heat-treatment. Hence we obtained single phase $Na_2FeP_2O_7$ from precursor glass. We also confirmed in previous study in the case of $LiFePO_4$ olivine phase from $Fe^{3+}$ rich precursor glass. We examine the cathode properties of $Na_2FeP_2O_7$ in sodium ion battery. The electrochemical reaction of $Na_2FeP_2O_7$ crystal is expressed as following equation

$$Na_2Fe^{(II)}P_2O_7 \rightarrow NaFe^{(III)}P_2O_7 + Na^+ + e^-. \qquad (1)$$
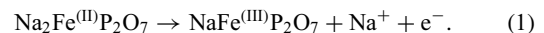
The theoretical capacity of Eq. (1) is estimated as 97 mAh/g. The charge–discharge curves during 10 cycles in 0.1 C are shown in **Fig. 4**. The initial discharge capacity is obtained as 88 mAh/g, which is corresponding to 90% for theoretical capacity. After 10 cycles the discharge capacity kept as 85 mAh/g. It is considered that reversible electro-chemical reaction is available as shown in Eq. (1). The principal plateau voltage exists at 2.9 V and another plateau was partially observed at 2.5 V. It seems that sodium ion site is classified as least two different sites as shown in Fig. 3 however the ionic conduction mechanism is not cleared. The principal sodium ion conduction in $Na_2FeP_2O_7$ crystal might be dominated by Na(1) which is exists opened tunnel structure in crystal. On the other hand Na(2) exists complicated sites in polyanion frame structure. We are going to clear the sodium ion conduction in near future.

## 4.   Conclusion

We fabricated $Na_2FeP_2O_7$ triclinic phase which working as cathode active materials in sodium ion battery by glass-ceramics

method. It cleared that Na$_2$FeP$_2$O$_7$ glass-ceramics shows the good electrochemical properties, which is almost same as theoretical discharge capacity with a good cycle performance. Although the energy density is lower than that of LiFePO$_4$, Na$_2$FeP$_2$O$_7$ glass-ceramics has huge advantages for the reducing materials cost.

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