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# Electrochemical Sodium Insertion into the 3D-framework of $\text{Na}_3\text{M}_2(\text{PO}_4)_3$ ( $\text{M} = \text{Fe}, \text{V}$ )

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Insertion of sodium into phosphates  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  ( $\text{M} = \text{Fe}, \text{V}$ ) were investigated electrochemically to determine the usefulness as the possible cathodes for sodium batteries. The discharge curves show that sodium ion can be accommodated into these hosts. Specific charges of up to  $45 \text{ mAhg}^{-1}$  and  $140 \text{ mAhg}^{-1}$  were obtained for  $\text{Na}/\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  and  $\text{Na}/\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cells with liquid organic electrolytes at room temperature, respectively. Intercalation processes under constant current densities of  $0.1 \text{ mAcm}^{-2}$  were reversible within the range of composition  $3.0 < x < 3.4$  for  $\text{Na}_x\text{Fe}_2(\text{PO}_4)_3$  and  $1.2 < x < 3.8$  for  $\text{Na}_x\text{V}_2(\text{PO}_4)_3$ .

## Introduction

Lithium transition metal dioxides with the general formula  $\text{LiMO}_2$  ( $\text{M} = \text{V}, \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}$ ) are seen to have the structure of  $\alpha$ - $\text{NaFeO}_2$ , which can be regarded as a distorted rock salt type structure.  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  used as cathodes for secondary lithium ion batteries have assumed an industrial importance<sup>1-6)</sup>. At the same time, a number of materials have been synthesized and evaluated for use as the cathode-active material in lithium secondary batteries. Examples of such materials include: spinel-type,  $\text{Li}_2\text{MMn}_3\text{O}_8$  and  $\text{LiM}'\text{MnO}_4$  ( $\text{M} = \text{Cr}$ <sup>7, 8)</sup>,  $\text{Fe}$ <sup>9)</sup>,  $\text{Co}$ <sup>10)</sup>,  $\text{Ni}$ <sup>11, 12)</sup>,  $\text{Cu}$ <sup>13, 14)</sup>;  $\text{M}' = \text{Cr}$ <sup>7, 8)</sup>,  $\text{Co}$ <sup>15)</sup>); inverse spinel-type,  $\text{LiMVO}_4$  [ $\text{M} = \text{Ni}, \text{Co}$ ]<sup>16)</sup>; layered-type,  $\text{LiMnO}_2$ <sup>17-19)</sup>; and so on.

The vast majority of studies have been directed toward the promising lithium system, but recent results obtained on  $\text{NaMO}_2$  ( $\text{M} = \text{Co}, \text{Ni}$ )<sup>20)</sup>,  $\alpha$ - $\text{MoO}_3$ <sup>21)</sup> and  $\text{NaTi}_2(\text{PO}_4)_3$ <sup>25)</sup> prove that sodium cells can function with liquid organic electrolytes at room temperature. However, improvement in energy density and rate capability is required for practical use of sodium batteries. Because of the lower capacity density and less negative voltage [vs. standard hydrogen electrode (SHE)] compared to lithium, energy densities are expected to be lower for cells utilizing sodium. Additionally, host materials commonly used as cathodes tend to intercalate sodium to a lesser extent than lithium due to the larger ionic radius, further reducing energy densities. Still, the comparatively lower cost of sodium<sup>22)</sup> makes development of sodium/liquid organic electrolyte systems a compelling goal (Table 1).

Clearly, the challenge is to find a cathode material that can intercalate sodium to a large extent and thus allow a high theoretical energy density in sodium batteries. Recently, polyanionic compounds that exhibit framework structures built up from both  $(\text{MO}_n)$  polyhedra and  $(\text{XO}_4)^m$ -tetrahedra polyanions ( $\text{M} = \text{transition metal}$ ;  $\text{X} = \text{S}$ <sup>23, 24)</sup>,  $\text{P}$ <sup>24)</sup>) instead of only  $(\text{MO}_n)$  polyhedra in transition oxides, have attracted considerable attention. The main reason is that lithium and sodium ions can both be inserted into a series of compounds having a general formula of  $\text{A}_x\text{M}_2(\text{XO}_4)_3$  ( $\text{A} = \text{Li}$  and  $\text{Na}$ ;  $\text{M} = \text{Ti}$ <sup>25)</sup>,  $\text{Fe}$ <sup>26)</sup>;  $\text{X} = \text{P}$ <sup>25)</sup>,  $\text{S}$ <sup>26)</sup>), because they have a large lithium or sodium site based on the 3D framework (Fig. 1). In addition, their operating voltage can be tuned by the crystal structure as well as by the choice of the counter-cation, X. It has been shown in previous works on  $\text{Li}_x\text{Fe}_2(\text{XO}_4)_3$  ( $\text{X} = \text{Mo}, \text{W}, \text{S}, \text{P}$ )<sup>27, 28)</sup> compounds that the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple lies at 3.0, 3.0, 3.6, and 2.8 V vs.  $\text{Li}/\text{Li}^+$ , and from the viewpoint of crystal structure, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple vs.  $\text{Li}/\text{Li}^+$  in four iron phosphates, NASICON-type  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ <sup>27)</sup>, the pyrophosphates  $\text{LiFeP}_2\text{O}_7$ <sup>27)</sup> and  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ <sup>27)</sup>, and olivine-type  $\text{LiFePO}_4$ <sup>27)</sup>, lies at 2.8, 2.9, 3.1, and 3.5 V, respectively. Although some of these phosphates and oxides, such as  $\text{NaTi}_2(\text{PO}_4)_3$  and  $\alpha$ - $\text{MoO}_3$ , are interesting as candidates for the high-voltage cathode material for sodium batteries, the gravimetric energy densities of those materials with liquid organic electrolytes at room temperature remain at 280 and 285  $\text{Whkg}^{-1}$ , respectively.

In the present study, we synthesized  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  ( $\text{M} = \text{Fe}, \text{V}$ ) phosphates by solid state reaction, and we paid attention not only to its open structure and flexibility but also to the possibility of reducing  $\text{M}^{3+}$  ( $\text{M} = \text{Fe}, \text{V}$ ) by eventual intercalation of sodium metal, and its potential for use as the new cathode material for sodium batteries was discussed.

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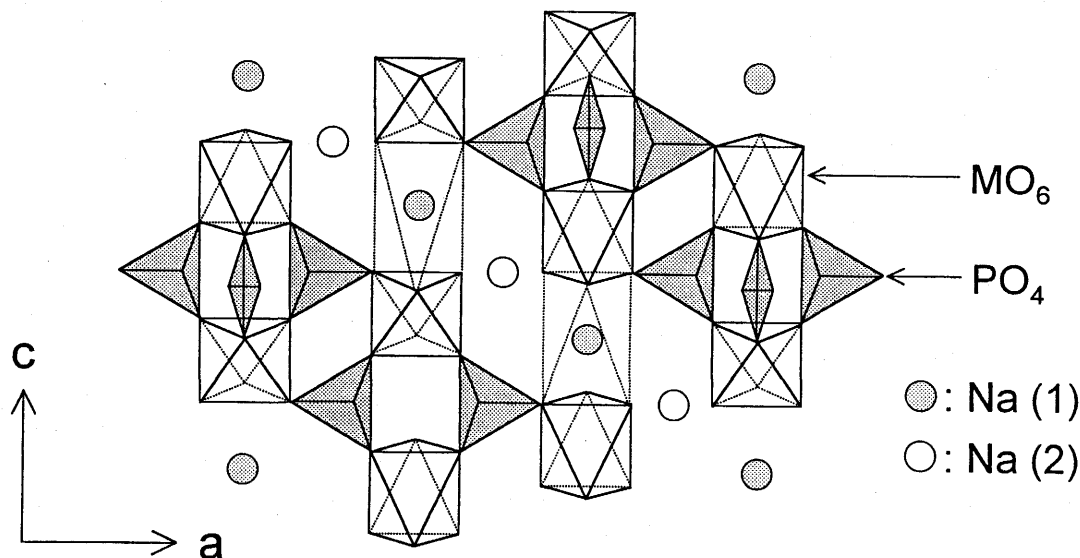


Fig. 1 Idealized representation of the rhombohedral form of the NASICON structure <sup>31)</sup>.

Table 1. Characteristics of anode materials.

Characteristic	Sodium	Lithium
Cost/equiv. (dollars) for Bulk metal	0.075	0.50
Capacity density (Ah g <sup>-1</sup> )	1.06	3.86
V vs. S. H. E.	-2.71	-3.05
Ionic radius (Å)	0.98	0.68

### Experiment

$\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M = Fe, V) powder samples were prepared by conventional solid reaction methods. Starting materials were  $\text{Na}_3\text{PO}_4$  (97 % Aldrich),  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  (Aldrich),  $\text{V}_2\text{O}_5$  (99.0% Rare Metallic Co., Ltd),  $\text{NaH}_2\text{PO}_4$  (99.0 % Kanto Chemical Co., Inc). These reagents were mixed;  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was heated under  $\text{Ar}/\text{H}_2$  (5 vol. %) flow at 900 °C for 12 – 36 h, and  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  was heated in air at 700 – 960 °C for 5 – 24 h. The obtained powder samples were identified by powder X-ray diffractometer (Rigaku RINT2100HLR/PC) with  $\text{Cu K}\alpha$  radiation. The samples for the electrochemical measurements were prepared by mixing crystalline  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M =Fe, V) powder samples, acetylene black as conductive agent and PTFE Teflon binder (70, 25 and 5 wt.%, respectively) in an agate mortar and were made in the form of sheet (1 mm thickness). The sheet was then cut into a disk form (15 mm diameter). Cells were fabricated by coupling this disk

with sodium foil with the same area as counter-electrode using microporous polypropylene film (Celgard 3501) as separator. (Fig. 2) 1M  $\text{NaClO}_4$  solution in propylene carbonate (PC) was used as the electrolytes. The electrochemical measurements were carried out galvanostatically with a current density of  $0.1\text{mAcm}^{-2}$  at room temperature. Correction of the line positions was carried out using silicon powder (NIST 640 c) as internal standard.

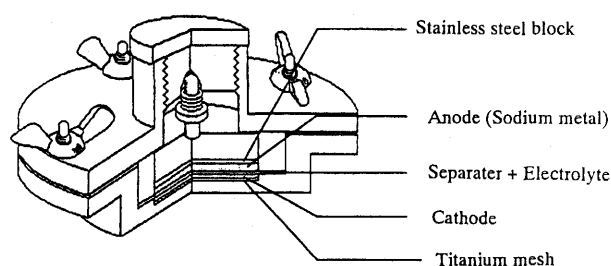


Fig. 2 Sodium cell construction.

### Results and Discussion

#### Synthesis

Figure. 3 showed the X-ray diffraction patterns of  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M = Fe, V) powder samples. On indexing the reflection peaks in the X-ray pattern of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  that was synthesized under  $\text{Ar}/\text{H}_2$  (5 vol. %) flow at 900 °C for 36 h, it was found that the sample has a rhombohedral

lattice. On the other hand, XRD peaks of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  that was synthesized in air at 960 °C for 24 h could be indexed by a monoclinic lattice. A cause for the differences of the crystal lattice may have been due to ionic radii in an octahedral oxide environment for iron and vanadium ( $r_{\text{Fe}^{3+}}^{\text{VI}}$ : 0.645 Å,  $r_{\text{V}^{5+}}^{\text{VI}}$ : 0.640 Å<sup>29</sup>). In comparison with the lattice parameters of this study and reported values for  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M = Fe<sup>30</sup>, V<sup>31</sup>), slight increase of *a* axis parameter for  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  was observed (Table 2).

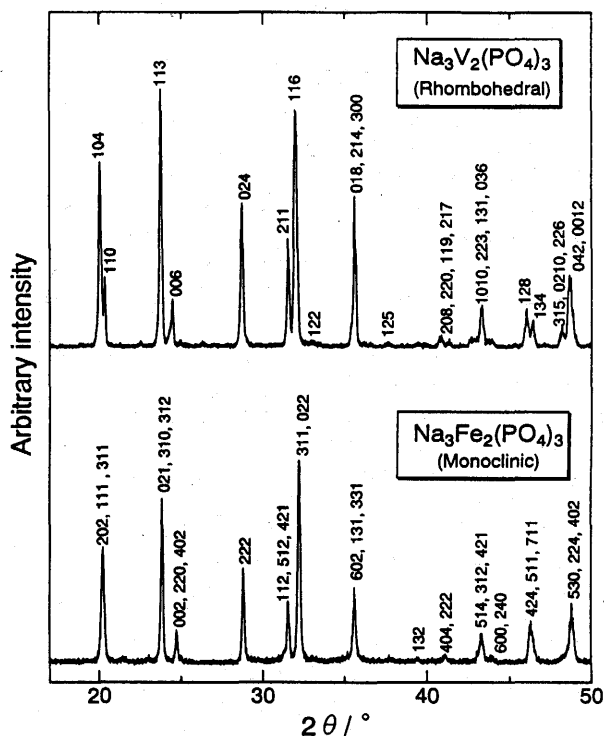


Fig. 3 X-ray diffraction patterns of  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M = Fe, V).

### Sodium insertion behavior

Figures 4 and 5 show the discharge and charge curves for Na/  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M = V, Fe) cells during the first cycle with a current density of 0.1 mAcm<sup>-2</sup> at room temperature in the voltage range of 1.2-3.5 V for M = V, and of 1.6-2.7 V for M = Fe, respectively. The sodium contents of materials indicated in the figures were calculated using the electric charge passed through the cell and the electrode active mass. Cell cycling began with sodium insertion for both samples. The insertion of sodium into

$\text{Na}_{3-x}\text{V}_2(\text{PO}_4)_3$  proceeded from *x* = 0 to 0.8 with a single-phase reaction which is indicated by slight slope around 1.5 V in discharge curve. The new slope around 3.3 V was observed in discharge curve after charged up to 3.5 V, and total discharge capacity for Na/  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cell was 140mAhg<sup>-1</sup>. On the other hand, Na/  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  cell showed only one slope around 2.5 V in discharge curve, and the discharge capacity for the first cycle was remain at 45mAhg<sup>-1</sup>. Figure 6 shows the reversible gravimetric energy density for the first cycle of Na/  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M = Fe, V),  $\text{NaMO}_2$  (M = Co, Ni)<sup>20</sup>,  $\alpha\text{-MoO}_3$ <sup>21</sup>, and  $\text{NaTi}_2(\text{PO}_4)_3$ <sup>25</sup>, which values were calculated from the capacity, average voltage, and true density data with liquid organic electrolytes at room temperature. However the discharge capacity of the Na/  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  cell remains at 45 mAhg<sup>-1</sup>, the Na/  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cell provides a higher gravimetric energy density than that of  $\text{NaMO}_2$  (M = Co, Ni),  $\text{Na}_x\text{MoO}_3$ , or  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ , though there is a big penalty in the form of the non-electroactive  $\text{PO}_4$  polyanion.

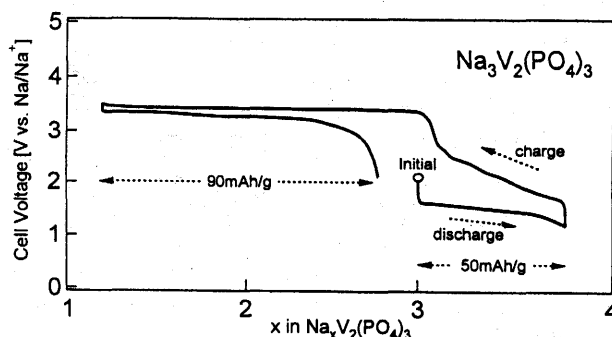


Fig. 4 Discharge and charge curves for Na/  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cell during the first cycle with a current density of 0.1 mAcm<sup>-2</sup> at room temperature in the voltage range of 1.2-3.5 V.

Table 2. Summary of calculated unit cells for  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  (M = Fe, V).

Compound	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)
$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ (Reported) <sup>a</sup>	15.14	8.73	8.80
(Monoclinic) (Observed)	15.13	8.71	8.80
$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (Reported) <sup>b</sup>	8.64	• • •	21.72
(Rhombohedral) (Observed)	8.71	• • •	21.73

a) From Ref. 30), b) From Ref. 31)

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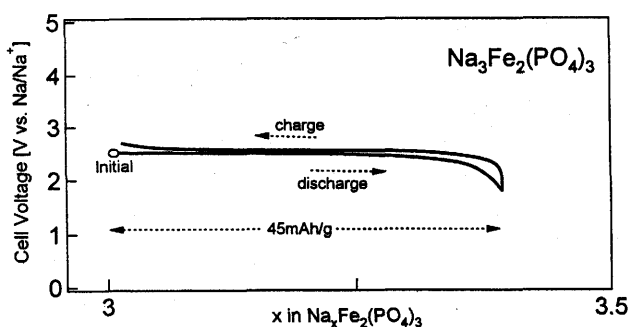


Fig. 5 Discharge and charge curves for Na/  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  cell during the first cycle with a current density of  $0.1 \text{ mAcm}^{-2}$  at room temperature in the voltage range of 1.6-2.7 V.

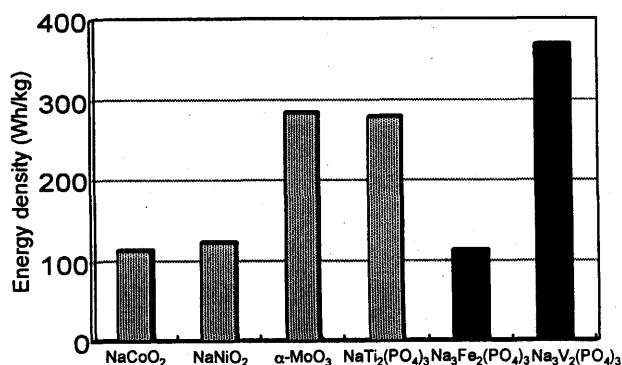


Fig. 6 Reversible gravimetric energy density for the first cycle of various cathode materials for sodium system with liquid organic electrolytes at room temperature.

## Conclusion

A study of the electrochemical sodium insertion in  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  ( $\text{M} = \text{Fe}, \text{V}$ ) with liquid organic electrolytes at room temperature was carried out. It revealed that  $\text{Na}_3\text{M}_2(\text{PO}_4)_3$  ( $\text{M} = \text{Fe}, \text{V}$ ) are suitable as cathode active materials for sodium insertion batteries. However the gravimetric energy density of the Na/ $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  cell was comparable to that of Na/ $\text{NaMO}_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ) cells (about  $120 \text{ Whkg}^{-1}$ ), the Na/ $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cell provides a higher gravimetric energy density than those of the present materials,  $\text{NaMO}_2$  ( $\text{M} = \text{Co}, \text{Ni}$ ),  $\text{Na}_x\text{MoO}_3$ , or  $\text{Na}_x\text{Ti}_2(\text{PO}_4)_3$ .

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