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# Synthesis, Structures, and Electrochemical Characteristics of Pyrophosphates

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We synthesized the two pyrophosphates  $\text{LiVP}_2\text{O}_7$  and  $\text{TiP}_2\text{O}_7$  by a solid state reaction, and the cathode properties of lithium secondary batteries were investigated. The structures were characterized by powder X-ray Rietveld refinement. Lithium cells using  $\text{LiVP}_2\text{O}_7$  and  $\text{TiP}_2\text{O}_7$  cathodes showed that approximately 0.5 Li per unit could be reversibly deintercalated from  $\text{LiVP}_2\text{O}_7$  at 4.1 V vs.  $\text{Li/Li}^+$ , 0.8 Li per unit could be reversibly intercalated into  $\text{TiP}_2\text{O}_7$  at 2.6 V vs.  $\text{Li/Li}^+$ . The redox potentials 4.1 V of  $\text{LiVP}_2\text{O}_7$  and 2.6 V of  $\text{TiP}_2\text{O}_7$  were higher than that of transition metal oxides such as  $\text{VO}_2$  and  $\text{TiO}_2$ .

## Introduction

Transition metal oxides, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$  have been investigated extensively as positive electrode materials for "rocking chair" batteries with carbon lithium negative electrodes<sup>1,2)</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. Recently, Goodenough *et al.* investigated polyanionic compounds that exhibit framework structures built up from both  $(\text{MO}_6)$  polyhedra (most often octahedra) and  $(\text{XO}_4)^{m-}$  tetrahedra polyanions ( $\text{M}$ = transition metal;  $\text{X}$  = P, S, V, As, Mo, W)<sup>3,4)</sup> instead of only  $(\text{MO}_6)$  polyhedra in transition oxides. Such structures can be viewed as obtained by the replacement of  $\text{O}^{2-}$  anions by larger size  $(\text{XO}_4)^{m-}$  polyanions. Well-known examples of such compounds are: phosphates such as olivine-type  $\text{LiFePO}_4$ <sup>3)</sup> or NASICON-type  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ <sup>3)</sup>, sulfates such as  $\text{Fe}_2(\text{SO}_4)_3$ <sup>5)</sup> or vanadates such as spinel-type  $\text{V}[\text{LiMn}]\text{O}_4$ <sup>6)</sup>.

The synthesis of new NASICON phosphates with mixed conductivity and the Na intercalation properties of such compounds have been studied since the early 90s<sup>7,8,9)</sup>. Li intercalation properties of such compounds have been known for more than ten years<sup>5,10,11)</sup>. Interest has been focused recently on polyanionic compounds as cathode materials of rechargeable Li batteries<sup>3,4,12,13)</sup>. These materials display lower theoretical specific capacities than transition metal oxides, because they contain a "dead mass" coming from the non-electroactive X cations that cannot store electrons. However, they are of high interest because their operating voltage can be monitored in the 2.5 - 4.0V range as a function of the nature of M and X

cations<sup>13)</sup>, the choice of the  $\text{M}^{\alpha+}/\text{M}^{(\alpha-1)+}$  redox system<sup>4)</sup> and the type of crystal structure<sup>3)</sup>. It has also been shown in previous works on  $\text{Li}_x\text{Fe}_2(\text{XO}_4)_3$  ( $\text{X}$  = Mo, W, S, P)<sup>3,4)</sup> compounds, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple lies at 3.0, 3.0, 3.6, and 2.8 eV vs.  $\text{Li/Li}^+$ . From a viewpoint of crystal structure, for example, the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox potential vs.  $\text{Li/Li}^+$  in four iron phosphates, NASICON-type  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ <sup>3)</sup>, the pyrophosphates  $\text{LiFeP}_2\text{O}_7$ <sup>3)</sup> and  $\text{Fe}_4(\text{P}_2\text{O}_7)_3$ <sup>3)</sup> and olivine-type  $\text{LiFePO}_4$ <sup>3)</sup> lies at 2.8, 2.9, 3.0, and 3.5 V; each of these materials has a specific capacity of about 100, 60, 110, and 160mAh/g.<sup>3)</sup>

Although all of these phosphates are used in low-cost, high-voltage rare-metal free cathodes, the theoretical capacity of pyrophosphate  $\text{Li}_{1+x}\text{FeP}_2\text{O}_7$  is especially small especially due to the large condensate  $\text{P}_2\text{O}_7$  polyanion. In order to improve the rechargeable capacity of this pyrophosphate, ion exchanges of Fe in  $\text{LiFeP}_2\text{O}_7$  were attempted using Ti or V in expectation of the reversible  $\text{M}^{4+}/\text{M}^{3+}$  redox reaction in addition to the  $\text{M}^{3+}/\text{M}^{2+}$  redox reaction.

In this study, a group of  $\text{Li}_x\text{MP}_2\text{O}_7$  ( $\text{M}$  = V, Ti) pyrophosphates with unknown crystal structures were synthesized and characterized by X-ray diffraction (XRD) measurements. To reveal lithium-insertion/extraction reaction, electrochemical characteristics were also investigated by galvanostatic method.

## Experiment

$\text{LiVP}_2\text{O}_7$  and  $\text{TiP}_2\text{O}_7$  were prepared by heating appropriate molar ratios of  $\text{Li}_2\text{CO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Ti}_2\text{O}_3$ , and  $\text{NH}_4\text{H}_2\text{PO}_4$  ( $\text{Li}_2\text{CO}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$ : Wako Chemical, > 99.0% purity;  $\text{V}_2\text{O}_5$ ,  $\text{Ti}_2\text{O}_3$ : Furuuchi Chemical, > 99.9% purity). These samples were mixed;  $\text{LiVP}_2\text{O}_7$  was fired under argon gas flow at 527K-1373K for 6-12h, and

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Dedicated to Professor Yukio Nishimura on the occasion of his retirement.

TiP<sub>2</sub>O<sub>7</sub> was fired in air at 973K for 12-24h.

X-ray diffraction (XRD) patterns of the powdered samples were obtained with an X-ray diffractometer (Rigaku RINT2100HLR/PC) with Cu K $\alpha$  radiation. The XRD data for Rietveld analysis were collected for 1-2 s at each 0.02° step width over a 2 $\theta$  range from 10 to 50°. The structural parameters were refined by Rietveld analysis using the computer program RIETAN97- $\beta$ <sup>14)</sup>. The Rietveld method furnishes the refined lattice parameters and structural parameters directly from whole powder diffraction patterns without separating reflections. This method is useful (I) when single crystals cannot be grown at all, (II) when only twinned samples can be prepared, and (III) when physical and/or chemical properties of single crystal forms differ from those of polycrystalline ones. Recently, the structures of many superconducting compounds were determined using neutron measurements and Rietveld method has been widely used to determine the structures of polycrystalline samples.

In the Rietveld analysis, the residual  $S_y$ , is minimized as the least squares refinement:

$$S_y = \sum w_i (y_i - y_{ci})^2$$

where

$$W_i = 1/y_i$$

$y_i$ : observed intensity at the  $i$  th step,

$y_{ci}$ : calculated intensity at the  $i$  th step,

and the sum is overall data points.

The calculated intensities  $y_i$  are determined from the  $F_K^2$  values calculated from the structural model by summing of the calculated contributions from neighboring Bragg reflections plus the background:

$$y_{ci} = s \sum L_K |F_K|^2 \rho(2\theta_i - 2\theta_k) P_K A + y_{bi}$$

where

$s$ : scale factor,

$K$ : Miller indices,  $h k l$ , for a Bragg reflection,

$L_K$ : Lorentz, polarization, and multiplicity factors,

$\rho$ : reflection profile function,

$P_K$ : preferred orientation function,

$A$ : absorption factor,

$F_K$ : structure factor for the  $k$  th Bragg reflection,

$y_{bi}$ : background intensity at the  $i$  th step.

The Rietveld refinement process will adjust the refinement parameters until the residual is minimized. The parameters,  $R_{WP}$ ,  $R_p$ ,  $R_1$ ,  $R_e$ , and etc., are suggested for the

indicators. Of these indicators, two indicators are important to judge whether the refinement is convoluted satisfactory.  $R_{WP}$  (weight pattern  $R$ -factor) is the most meaningful of these  $R$  because the numerator is the residual being minimized. Another useful numerical criterion is the goodness of fit,  $S$  ( $=R_{WP}/R_e$ ).

$$R_{WP} = \left| \frac{\sum_i w_i (y_i - f_{ci})^2}{\sum_i w_i y_i^2} \right|^{\frac{1}{2}}$$

$$R_e = \left| \frac{N_p - N_r - N_c}{\sum_i w_i y_i^2} \right|^{\frac{1}{2}}$$

$$S = \left| \frac{\sum_i w_i (y_i - y_{ci})^2}{N_p - N_r - N_c} \right|^{\frac{1}{2}}$$

Where

$N_p$ : number of strength datum,

$N_r$ : number of parameters that will refinement,

$N_c$ : number of restrictions.

Electrochemical intercalation and de-intercalation were carried out using lithium cells. The working electrode consisted of a mixture of 75mg samples, 25mg acetylene black (Denki Kagaku Co. Ltd.) and 0.3mg F-210L PTFE Teflon binder (Daikin Industry Ltd.) pressed into a tablet of 15mm diameter under a pressure of 10Mpa. The cells used for the electrochemical tests were constructed in a stainless steel 2032 coin-type configuration (20mm outside diameter and 3.2 mm thickness). The counter electrode was a 15mm diameter and 1.0mm thickness disk of lithium metal foil. The electrolytes we used consisted of a 1 M solutions of LiPF<sub>6</sub> in a 50:50 vol.% mixture of ethylene carbonate (EC) and 1,2 dimethoxycarbonate (DMC) (Tomiyama Co. Ltd.). A microporous polypropylene film (Celgard 3501) was used as a separator. The cell construction was indicated in Fig. 1. The cell was assembled in a argon atmosphere (the dew point was less than -70°C). The current density was calculated based on the cathode area. The electrochemical measurements were carried out at room temperature after standing overnight under zero current flow.

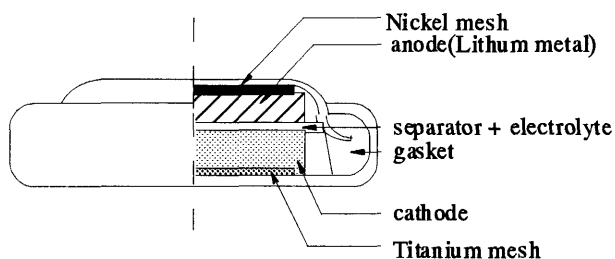


Fig. 1 Lithium cell construction.

## Results and Discussion

### Synthesis and structures

On indexing the reflection peaks in the powder X-ray pattern of  $\text{LiVP}_2\text{O}_7$  that was synthesized under argon gas flow at 1373K for 12h, it was found that the sample has a single phase with a monoclinic lattice. We attempted to refine the structure of  $\text{LiVP}_2\text{O}_7$  using space groups by the Rietveld method. The structure was refined with space group  $P2_1$  using a structural model reported by Riou *et al.*<sup>15)</sup>, that is built up from corner-sharing  $\text{VO}_6$  octahedra and  $\text{P}_2\text{O}_7$  groups. The tunnels result from stacking of rings formed by the edges of three octahedra and four tetrahedra. The overall thermal parameters  $B$  for all sites were constrained to be the same value. The lattice parameters was indexed by a monoclinic cell with  $a = 4.8102(7)\text{Å}$ ,  $b = 8.1208(5)\text{Å}$ ,  $c = 6.9465(10)\text{Å}$ ,  $\beta = 109.006(10)^\circ$ .

On the other hand,  $\text{TiP}_2\text{O}_7$  was synthesized in air at 973K for 24h. Approximate XRD peaks could be indexed by a cubic lattice similar to that of  $\text{ZrV}_2\text{O}_7$ <sup>16)</sup> that show complex patterns consistent with the  $Pa3$  space group and the  $3 \times 3 \times 3$  superstructure, that is built up from corner-sharing  $\text{ZrO}_6$  octahedra and  $\text{V}_2\text{O}_7$  groups. The lattice parameters was indexed by a cubic cell with  $a = 23.626(4)\text{Å}$ ,  $Z = 108$ . The structures of  $\text{LiVP}_2\text{O}_7$  and  $\text{TiP}_2\text{O}_7$  that had been calculated by Rietveld refinement was indicated in Fig. 2(a), (b). The fitting patterns refined best on space group are illustrated in Fig. 3(a), (b). The final  $R$  factors, lattice and structural parameters, and their estimated standard deviations were listed on Table 1-2.

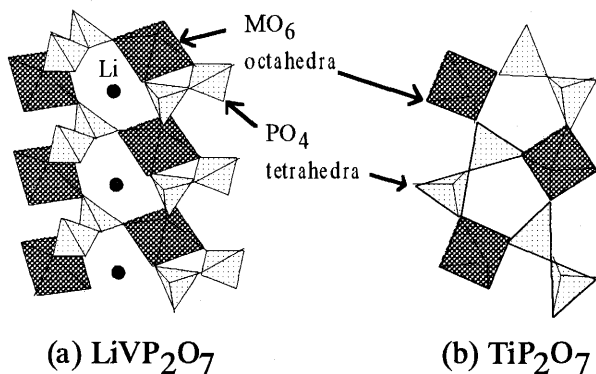


Fig. 2 Crystal structures of (a):  $\text{LiVP}_2\text{O}_7$  and (b):  $\text{TiP}_2\text{O}_7$ .

Table 1 X-ray Rietveld refinement results for monoclinic  $\text{LiVP}_2\text{O}_7$ .<sup>a</sup>

| Atom | x        | y        | z         | $B(\text{Å}^2)$ |
|------|----------|----------|-----------|-----------------|
| Li   | 0.803(2) | 0.384(3) | 0.819(2)  | $B(\text{V})$   |
| V    | 0.213(7) | 0.236(4) | 0.228(8)  | 0.47(2)         |
| P(1) | 0.789(7) | 0.455(2) | 0.415(13) | $B(\text{V})$   |
| P(2) | 0.602(8) | 0.051(6) | 0.981(5)  | $B(\text{V})$   |
| O(1) | 0.396(2) | 0.079(6) | 0.109(7)  | $B(\text{V})$   |
| O(2) | 0.801(2) | 0.209(6) | 0.019(16) | $B(\text{V})$   |
| O(3) | 0.134(7) | 0.056(6) | 0.384(3)  | $B(\text{V})$   |
| O(4) | 0.049(4) | 0.423(6) | 0.356(5)  | $B(\text{V})$   |
| O(5) | 0.244(7) | 0.394(4) | 0.011(17) | $B(\text{V})$   |
| O(6) | 0.389(3) | 0.100(5) | 0.750(5)  | $B(\text{V})$   |
| O(7) | 0.604(3) | 0.319(8) | 0.413(4)  | $B(\text{V})$   |

<sup>a</sup> Space group:  $P2_1$ ;  $a=4.8102(7)\text{Å}$ ;  $b=8.1208(5)\text{Å}$ ;  $c=6.9465(10)\text{Å}$ ;  $\beta=109.006(10)^\circ$ ;  $R_{\text{wp}}=14.13\%$ ;  $R_c=8.76\%$ ;  $R_1=4.06\%$ , and  $S=1.6137$ .

Table 2 X-ray Rietveld refinement results for cubic  $\text{TiP}_2\text{O}_7$ .<sup>b</sup>

| Atom  | x         | y         | z         | $B(\text{Å}^2)$  |
|-------|-----------|-----------|-----------|------------------|
| Ti(1) | 0.323(3)  | -0.004(6) | 0.986(3)  | 0.7(2)           |
| Ti(2) | 0.334(18) | 0.350(8)  | 0.001(9)  | $=B(\text{Ti1})$ |
| Ti(3) | 0.999(6)  | 0.333(4)  | 0.642(6)  | $=B(\text{Ti1})$ |
| Ti(4) | 0.338(9)  | 0.666(3)  | 0.335(9)  | $=B(\text{Ti1})$ |
| Ti(5) | 0.368(4)  | 0.368(4)  | 0.368(4)  | $=B(\text{Ti1})$ |
| Ti(6) | 0.000     | 0.000     | 0.000     | $=B(\text{Ti1})$ |
| P(1)  | 0.458(7)  | 0.121(7)  | 0.148(7)  | $=B(\text{Ti1})$ |
| P(2)  | 0.602(8)  | 0.051(6)  | 0.981(5)  | $=B(\text{Ti1})$ |
| P(3)  | 0.786(6)  | 0.127(5)  | 0.144(16) | $=B(\text{Ti1})$ |
| P(4)  | 0.779(8)  | 0.787(8)  | 0.158(16) | $=B(\text{Ti1})$ |
| P(5)  | 0.135(7)  | 0.473(9)  | 0.794(6)  | $=B(\text{Ti1})$ |
| P(6)  | 0.129(10) | 0.789(2)  | 0.468(2)  | $=B(\text{Ti1})$ |
| P(7)  | 0.452(5)  | 0.797(5)  | 0.445(7)  | $=B(\text{Ti1})$ |
| P(8)  | 0.479(3)  | 0.808(4)  | 0.781(2)  | $=B(\text{Ti1})$ |
| P(9)  | 0.823(8)  | 0.823(8)  | 0.823(8)  | $=B(\text{Ti1})$ |
| P(10) | 0.457(8)  | 0.457(8)  | 0.457(8)  | $=B(\text{Ti1})$ |
| P(11) | 0.104(13) | 0.130(7)  | 0.141(6)  | $=B(\text{Ti1})$ |
| O(1)  | 0.516(9)  | 0.181(8)  | 0.157(5)  | $=B(\text{Ti1})$ |
| O(2)  | 0.847(8)  | 0.149(7)  | 0.164(5)  | $=B(\text{Ti1})$ |
| O(3)  | 0.499(7)  | 0.494(2)  | 0.192(13) | $=B(\text{Ti1})$ |
| O(4)  | 0.049(4)  | 0.423(6)  | 0.356(5)  | $=B(\text{Ti1})$ |
| O(5)  | 0.162(7)  | 0.162(7)  | 0.162(7)  | $=B(\text{Ti1})$ |
| O(6)  | 0.500     | 0.500     | 0.500     | $=B(\text{Ti1})$ |
| O(7)  | 0.222(18) | -0.001(6) | 0.164(9)  | $=B(\text{Ti1})$ |
| O(8)  | 0.478(5)  | 0.083(5)  | 0.146(2)  | $=B(\text{Ti1})$ |
| O(9)  | 0.148(5)  | 0.406(7)  | 0.132(8)  | $=B(\text{Ti1})$ |
| O(10) | 0.142(3)  | 0.070(12) | 0.485(17) | $=B(\text{Ti1})$ |
| O(11) | 0.483(8)  | 0.404(9)  | 0.135(18) | $=B(\text{Ti1})$ |
| O(12) | 0.464(3)  | 0.075(4)  | 0.466(2)  | $=B(\text{Ti1})$ |
| O(13) | 0.154(6)  | 0.398(9)  | 0.461(6)  | $=B(\text{Ti1})$ |
| O(14) | 0.490(9)  | 0.361(3)  | 0.460(6)  | $=B(\text{Ti1})$ |
| O(15) | 0.811(8)  | 0.086(2)  | 0.143(9)  | $=B(\text{Ti1})$ |
| O(16) | 0.146(7)  | 0.731(2)  | 0.128(2)  | $=B(\text{Ti1})$ |
| O(17) | 0.148(3)  | 0.071(8)  | 0.805(9)  | $=B(\text{Ti1})$ |

|       |           |           |           |         |
|-------|-----------|-----------|-----------|---------|
| O(18) | 0.807(6)  | 0.751(4)  | 0.133(3)  | =B(Ti1) |
| O(19) | 0.818(5)  | 0.067(8)  | 0.777(14) | =B(Ti1) |
| O(20) | 0.122(18) | 0.794(18) | 0.808(6)  | =B(Ti1) |
| O(21) | 0.834(4)  | 0.689(6)  | 0.829(69) | =B(Ti1) |
| O(22) | 0.122(9)  | 0.389(11) | 0.813(9)  | =B(Ti1) |
| O(23) | 0.147(16) | 0.740(5)  | 0.468(4)  | =B(Ti1) |
| O(24) | 0.487(6)  | 0.740(7)  | 0.157(2)  | =B(Ti1) |
| O(25) | 0.477(3)  | 0.699(7)  | 0.558(7)  | =B(Ti1) |
| O(26) | 0.480(2)  | 0.401(3)  | 0.820(11) | =B(Ti1) |
| O(27) | 0.492(7)  | 0.736(2)  | 0.795(9)  | =B(Ti1) |
| O(28) | 0.490(8)  | 0.073(6)  | 0.793(8)  | =B(Ti1) |
| O(29) | 0.796(2)  | 0.092(3)  | 0.477(8)  | =B(Ti1) |
| O(30) | 0.817(3)  | 0.443(2)  | 0.145(3)  | =B(Ti1) |
| O(31) | 0.796(9)  | 0.397(5)  | 0.469(3)  | =B(Ti1) |
| O(32) | 0.799(4)  | 0.400(4)  | 0.780(7)  | =B(Ti1) |
| O(33) | 0.821(5)  | 0.745(4)  | 0.462(9)  | =B(Ti1) |

<sup>b</sup> Space group:  $Pa\bar{3}$ ;  $a=23.626(4)\text{\AA}$ ;  $R_{wp}=11.97\%$ ;  $R_e=6.32\%$ , and  $S=1.8927$ .

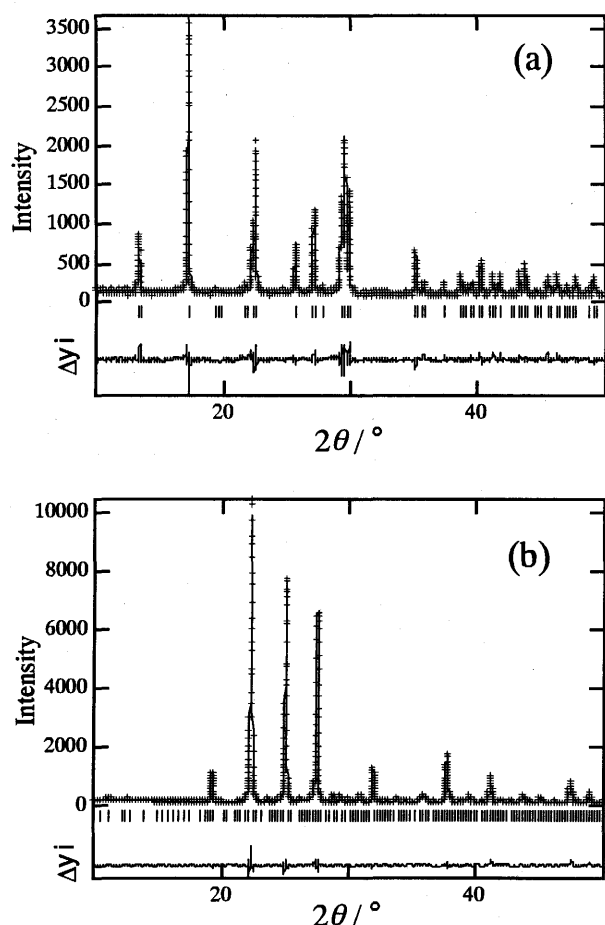


Fig. 3 Observed, calculated and difference plots for X-ray diffraction patterns of (a):  $\text{LiVP}_2\text{O}_7$  and (b):  $\text{TiP}_2\text{O}_7$ . The solid line is calculated intensity, dots overlying them are observed intensity, and  $\Delta y_i$  is the difference between observed and calculated intensity.

### Electrochemical properties

Fig. 4-5 showed a quasi-open circuit voltage curves for a  $\text{Li}/\text{LiVP}_2\text{O}_7$  and  $\text{Li}/\text{TiP}_2\text{O}_7$  cell. The quasi-open circuit voltage (QOCV) was measured after cell had been standing for 30 minutes at zero current flow for every 0.025 Li/mol depth of charge and discharge at  $0.2\text{mA}/\text{cm}^2$ . The lithium content of material indicated in the figure was calculated from electrochemically. In the case of  $\text{LiVP}_2\text{O}_7$ , cell cycling began with lithium extraction, because this sample has lithium ions in the matrix. The extraction of lithium from  $\text{Li}_{1-x}\text{VP}_2\text{O}_7$  proceeded from  $x = 0$  to 0.6 with a two-phase reaction which is indicated by the flat charge curve. The curve showed a slope change around  $x = 0.6$  to 1.0, which suggests a change in the de-intercalation mechanism. And the compound shows plateau around 4.1V vs.  $\text{Li}/\text{Li}^+$  upon discharging. The charge capacity for the first cycle was 115mAh/g, and the discharge capacity was 60mAh/g. The capacity loss could be caused by a decomposition of the electrolytes or a decomposition of the structure of  $\text{LiVP}_2\text{O}_7$  after the first charge cycle. On the other hand, cell cycling of  $\text{TiP}_2\text{O}_7$  began with lithium insertion, because this sample has no lithium ions in the matrix.  $\text{Li}/\text{TiP}_2\text{O}_7$  cell showed plateau that was caused by two-phase reaction around 2.6V vs.  $\text{Li}/\text{Li}^+$  upon discharging. The discharge capacity for the first cycle was 95mAh/g, and the obtained capacity loss was not much greater than that for the  $\text{Li}/\text{LiVP}_2\text{O}_7$  cell. Although the obtained capacities were lower than expected for large reversible capacity of more than 1Li per in  $\text{LiMP}_2\text{O}_7$ , it is noteworthy that the redox potentials 4.1 V of  $\text{LiVP}_2\text{O}_7$  and 2.6 V of  $\text{TiP}_2\text{O}_7$  were higher than that of transition metal oxides. For example, the redox potentials of  $\text{V}^{4+}/\text{V}^{3+}$  in  $\text{VO}_2^{17)}$  is 2.5 V, and that of  $\text{Ti}^{4+}/\text{Ti}^{3+}$  in  $\text{TiO}_2^{17)}$  is 1.8 V.

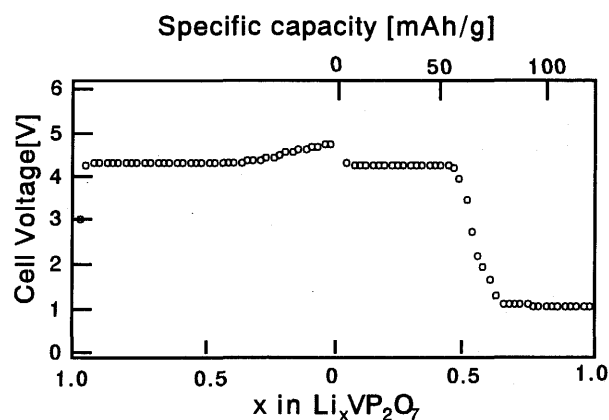


Fig. 4 Quasi-open circuit voltage profile of  $\text{LiVP}_2\text{O}_7$ .

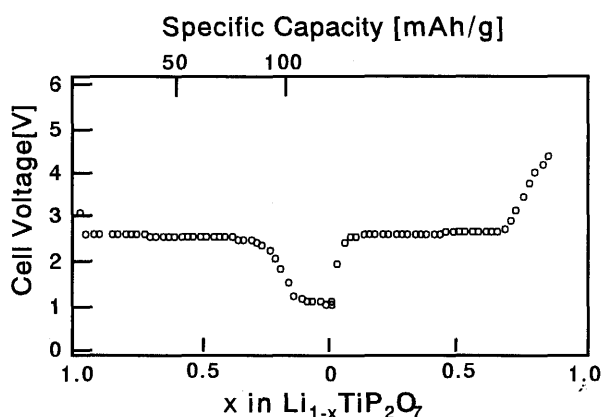


Fig. 5 Quasi-open circuit voltage profile of  $\text{TiP}_2\text{O}_7$ .

### Conclusion

Two pyrophosphates  $\text{LiVP}_2\text{O}_7$  and  $\text{TiP}_2\text{O}_7$  were prepared by a solid state reaction. We made two crystal structures clear by Rietveld refinement. The structure of  $\text{LiVP}_2\text{O}_7$  was isostructural with  $P2_1$  monoclinic  $\text{LiFeP}_2\text{O}_7$ , with  $a = 4.8102(7) \text{ \AA}$ ,  $b = 8.1208(5) \text{ \AA}$ ,  $c = 6.9465(10) \text{ \AA}$ , and  $\beta = 109.006(10)^\circ$ . On the other hand,  $\text{TiP}_2\text{O}_7$  was isostructural with  $Pa3$  cubic  $\text{ZrV}_2\text{O}_7$ , with  $a = 23.626(4) \text{ \AA}$ . Both structures consist of corner-sharing  $\text{MO}_6$  octahedra and  $\text{P}_2\text{O}_7$  diphosphates. Electrochemical measurements revealed that the two pyrophosphates were suitable as cathode active materials for lithium secondary batteries, and that the redox potentials in these pyrophosphates were higher than that of transition metal oxides such as  $\text{TiO}_2$  and  $\text{VO}_2$ .

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