Investigation of oxidation progress and structural change in hydrous iron phosphates, vivianite and santabarbaraite, by Li-intercalation

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Vivianite is a hydrous iron (II)-phosphate mineral with a chemical composition, Fe$^{2+}$$_4$(PO$_4$)$_2$·8H$_2$O. Fe$^{2+}$ in the vivianite structure can be partially oxidized by the deprotonation of water molecules; Fe$^{3+}$ + H$_2$O → Fe$^{3+}$ + OH$^-$ [1]. This oxidation further progresses in heating and parent vivianite turns into a disordered phase of santabarbaraite at around 120 °C [1, 2]. Although the structure of santabarbaraite has not yet been elucidated, the overall structural characteristics of santabarbaraite are similar to the crystal structure of vivianite (Fig. 1 (a), [3]). Additionally, the structure of santabarbaraite would have porous nature compared to vivianite, since santabarbaraite is a low-temperature dehydration product [3]. We investigated lithium intercalation (Fe$^{3+}$ + e$^-+ Li^+→Fe^{2+}Li^+$) into santabarbaraite, focusing on its oxidation state of Fe and structure.

Santabarbaraite was prepared by heating synthesized vivianite in the air at 120 °C for 2 hours [4]. Li-intercalation into the synthesized vivianite was also investigated to compare the performance of iron phosphates (partially oxidized vivianite and santabarbaraite) as cathode active materials. For the Li-intercalation test, an ordinary two-electrode cell was employed: the active material applied on an Al foil (30 μm) was a mixture of iron phosphate, carbon black, and polyvinylidene fluoride in the ratio of 8:1:1 by weight. The composite electrode was used as the working electrode, the Li metal plate as the reference and counter electrode, and a commercial electrolyte solution of 1M LiPF$_6$ in a solution of ethylene carbonate and dimethyl carbonate (1:1 by volume). The electrochemical reaction involved a constant-current-constant-voltage discharge and charge process (cut-off voltage was set to 2.0 V for discharge and 4.0 V for charge).

The results of electrochemical reaction are shown in Fig. 1 (b). Blue and red curves correspond to the results for the synthesized vivianite and santabarbaraite, respectively. The total amount of intercalated Li in the santabarbaraite-electrode was two times larger than that of the vivianite-electrode (in a cathodic capacity, santabarbaraite: 156 mAh$^-$ and vivianite: 70.9 mAh$^-$). This is because the total amount of Fe$^{3+}$ of santabarbaraite is larger than that of vivianite. Additionally, in the constant-current discharge process, the vivianite-electrode reached the cut-off voltage of 2.0 V immediately compared to the santabarbaraite-electrode. This result is due to a significantly low reaction rate of Li-intercalation in vivianite; the reaction rate is dominated by two factors, electron conductivity and Li$^+$ diffusivity. The electron conductivity of vivianite is larger than that of santabarbaraite, since santabarbaraite includes structural disorder [4]. On the other hand, santabarbaraite would have more space for Li diffusivity, since the number of water molecules decreases in santabarbaraite due to the dehydration. The higher reaction rate of santabarbaraite was owing to the Li diffusivity. Therefore, santabarbaraite is a suitable active material compared to vivianite in terms of the capacity and reaction rate.

In our presentation, structural change of the iron phosphates induced by Li-intercalation will be also discussed based on powder X-ray diffraction measurements.

![Figure 1.](image) (a) Schematic drawing of Li-intercalation in vivianite (santabarbaraite) (b) Discharge/charge curves of as synthesized vivianite and 120 °C heated santabarbaraite.


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