



Iron phosphide as negative electrode material for Na-ion batteries



Wanjie Zhang^a, Mouad Dahbi^{a,b}, Shota Amagasa^a, Yasuhiro Yamada^a, Shinichi Komaba^{a,b,*}

^a Tokyo University of Science, Shinjuku, Tokyo 162-8601, Japan

^b Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Kyoto 615-8245, Japan

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ABSTRACT

Iron phosphides, FeP₂ and FeP₄, have been synthesized and characterized for the application to non-aqueous Na-ion battery. FeP₂ shows no significant electrochemical reactivity in Na-cell. However, FeP₄ composite electrode with sodium polyacrylate binder delivers a reversible capacity of 1137 mAh·g⁻¹ and a Coulombic efficiency of 84.0% during the first cycle under a current density of 89 mA·g⁻¹. The high capacity is maintained for 30 cycles. Moreover, FeP₄ composite electrode presents a good rate capability. Although the sodiation mechanism of FeP₄ has not been fully understood, FeP₄ is a new promising negative electrode material for Na-ion batteries with both high-power and high-energy densities.

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1. Introduction

In the recent developments for Na-ion batteries, negative electrode made of red phosphorus, which enables three-electron reversible redox with Na, has been reported to present a reversible capacity for more than 2000 mAh·g⁻¹ [1,2]. However, the low electrical conductivity of red phosphorus, $<1 \times 10^{-14} \text{ S} \cdot \text{cm}^{-1}$ [3], has detrimental effects on its electrochemical performance [1].

On the other hand, over the past decades, conversion materials have been extensively studied in the research field of Li-ion batteries as potential replacements of insertion materials. Compared to the insertion mechanism, conversion reaction allows more electrons to participate in the electrochemical reaction, resulting in much higher reversible capacities. Among conversion materials, metal phosphides, such as NiP₃ [4], Sn₄P₃ [5,6], CuP₂ [7], FeP [8], and CoP [9] have been also reported to electrochemically react with Na through conversion mechanism, leading to the formation of Na₃P and nanosized metallic particles, creating a conductive network which supports good electrical conduction inside the electrode upon cycling [5].

Particularly, as iron is the most abundant d-block element, the comparatively low-cost iron phosphides are highly desirable to meet the future request of large-format battery. Therefore, our major interest lies on the application of conversion reaction of iron phosphides in Na-ion batteries. Indeed, intrinsic drawbacks of conversion materials should be always considered, such as severe volume change during sodiation/desodiation, large voltage hysteresis, and large irreversible capacity loss during the first cycles.

Moreover, in order to improve the cycling performance of electrode materials, apart from electrolyte additive, e.g. fluoroethylene carbonate (FEC) [2,6,10], considerable interest has also been revived in polymer binders, especially for the materials with high volume change. As we recently reported, sodium polyacrylate (PANA) binder highly enhances the capacity retention and cycle life of Si in Li-cell [11], tin [12] and red phosphorus [2] electrodes in Na-cell, compared with conventional poly(vinylidene fluoride) (PVdF) binder.

In the present work, we report the synthesis of iron phosphides, FeP₂ and FeP₄, by simple ball milling of iron and red phosphorus mixture and their electrochemical performances in Na-cell. In particular, the composite electrode based-on phosphorus-rich phase (FeP₄) demonstrates highly reversible sodiation capacity for high-energy Na-ion batteries.

2. Experimental

Iron phosphides (FeP_x, x = 2, 4) were mechanochemically synthesized from commercial sources. Red phosphorus powder (Sigma-Aldrich) and iron powder (Kojundo Chemical Laboratory) were mixed with two different P:Fe stoichiometric molar ratios, 2:1 and 4:1. Synthesis of active material was carried out in planetary ball milling (Pulverisette 7, Fritsch) for 30 h at 600 rpm under argon atmosphere using ZrO₂ jar and balls, the weight ratio of powder to ball is 1:17. Every 30 min of ball milling was followed by a 15 min break in order to release the heat.

Acetylene black (AB, Wako Pure Chemical Industries) as conductive additive and PANA (Kishida Chem.) as binder were mixed together with the phosphide in a mortar for 20 min. The slurry was prepared with deionized water and then cast on an aluminum foil as current collector and dried first at 80 °C in air for 2 h and then at 80 °C under vacuum for 12 h. The ratio of FeP_x:AB:PANA composite electrodes was

* Corresponding author at: Tokyo University of Science, Shinjuku, Tokyo 162-8601, Japan.

E-mail address: komaba@rs.kagu.tus.ac.jp (S. Komaba).

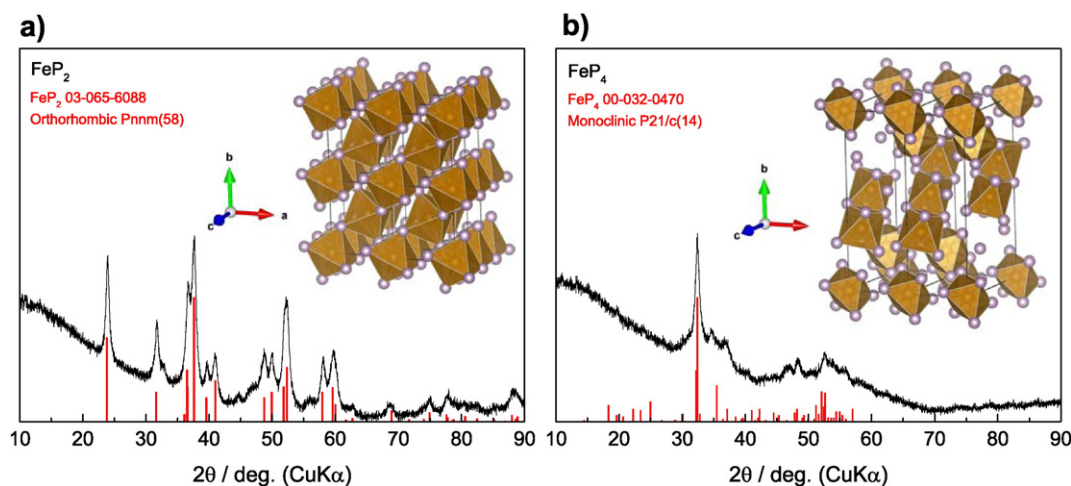


Fig. 1. XRD patterns of synthesized a) FeP_2 and b) FeP_4 , with their corresponding crystal structure.

70:10:20 or 60:20:20 (in weight). The loading of active material was $0.15\text{--}0.9\text{ mg}\cdot\text{cm}^{-2}$, and the total loading of electrode material was $0.2\text{--}1.3\text{ mg}\cdot\text{cm}^{-2}$ including AB and PANa.

Coin-type cells (R2032-type) were assembled with composite electrodes and sodium foil inside an argon-filled glovebox. Electrolyte solution used in this study was $1.0\text{ mol}\cdot\text{dm}^{-3}$ NaPF_6 in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (Kishida Chem.) with 2 vol.% additive FEC (Kanto Denka Kogyo). Glass filter (GB-100R, ADVANTEC) together with polyolefin porous membrane was applied as separator. The electrode was charged (sodiated) as negative electrode in Na-cell down to 0.05 V at C/20 ($1\text{C} = 1789\text{ mA}\cdot\text{g}^{-1}$) under constant current and kept at 0.05 V for 5 h, then

discharged (desodiated) up to 2.0 V under the same rate with battery tester (TOSCAT-3100, Toyo System). Rate capability test of desodiation (discharge) was performed using a same type coin cell on a VMP3 multi-channel potentiostat (BioLogic) with a sodiation rate fixed at C/20.

Phase identification was carried out by X-ray diffraction (XRD) (MultiFlex, Rigaku) equipped with a high-speed, one-dimensional X-ray detector (D/teX Ultra, Rigaku). Non-monochromatized $\text{Cu K}\alpha$ radiation was applied as the X-ray source with a nickel filter. Sample holders for XRD were equipped with small compartments to avoid any exposure from air during the experiments. ^{57}Fe Mössbauer spectra of the samples at room temperature (293 K) were collected in a

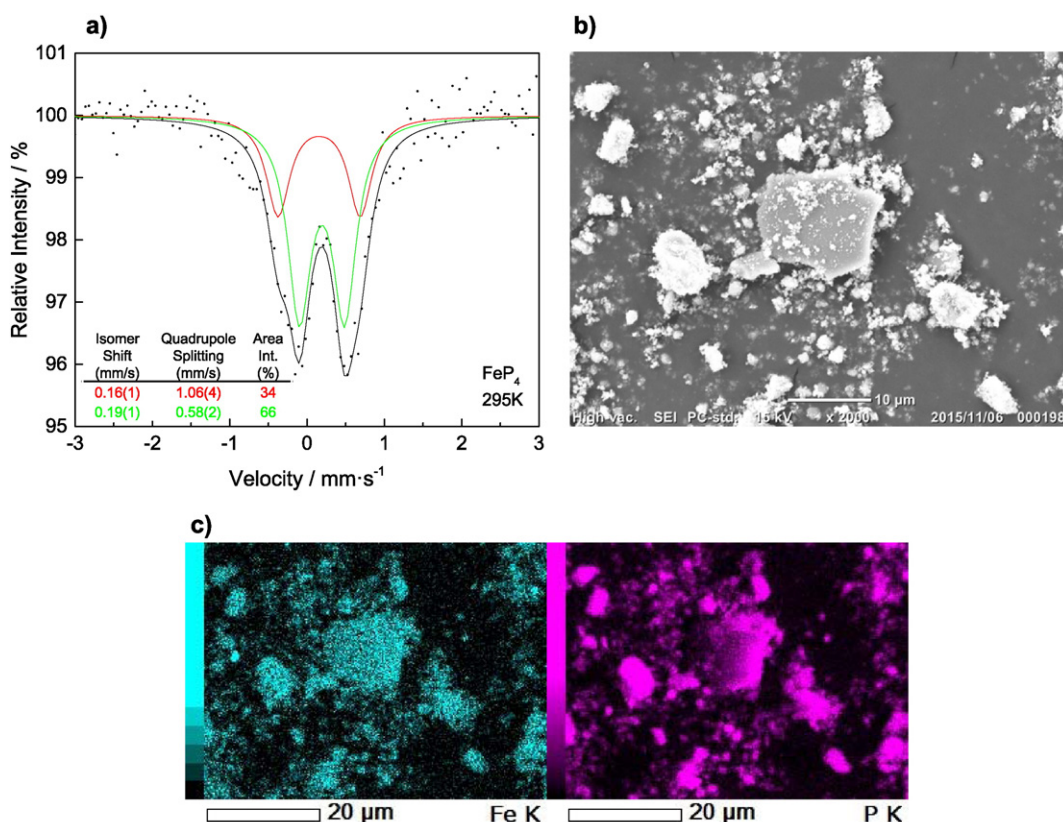


Fig. 2. a) Mössbauer spectrum of FeP_4 pristine electrode at 295 K, b) SEM image of FeP_4 particles, and c) the corresponding EDS mapping.

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