

Short communication

# Lithium insertion chemistry of phosphate phases with the lipscombite structure

Mickael Dollé, Sébastien Patoux, Thomas J. Richardson\*

*Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

Received 18 November 2004; accepted 15 December 2004

Available online 19 February 2005

## Abstract

The lithium insertion chemistry of an iron phosphate with the lipscombite structure,  $\text{Fe}_{1.19}\text{PO}_4\text{F}_{0.11}(\text{OH})_{0.46}(\text{H}_2\text{O})_{0.43}$ , was investigated by X-ray diffraction (XRD), galvanostatic cycling, and potentiostatic intermittent titration. The compound, prepared by a simple hydrothermal method, contains interconnecting chains of face-sharing  $\text{FeO}_6$  octahedra with about 60% Fe occupancy. Assuming that all the iron may be reduced, the theoretical capacity is about  $180 \text{ mAh g}^{-1}$ , similar to that of olivine-type  $\text{LiFePO}_4$ . Reversible intercalation was found to proceed via a single-phase reaction at an average potential of 2.8 V versus  $\text{Li}^+/\text{Li}$ . Good structural stability upon intercalation/deintercalation was observed. The unit cell volume increased linearly and isotropically with increasing lithium content, reaching 10% for a Li:Fe ratio of 0.96. XRD peak widths increased on lithiation, presumably due to disorder created by conversion of  $\text{Fe}^{3+}$  to the larger  $\text{Fe}^{2+}$ , but decreased on subsequent delithiation. The rate capability of this material appears to be diffusion-limited, and may benefit from a decrease in particle size. The lithium insertion behavior of a related compound,  $\text{Ti}_5\text{O}_4(\text{PO}_4)_4$ , was also investigated.

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**Keywords:** Lithium batteries; Iron phosphate; Intercalation compounds

## 1. Introduction

In recent years, considerable attention has been devoted to complex oxides containing three-dimensional polyanion frameworks such as olivine-type  $\text{LiFePO}_4$  and NaSiCON-type  $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ , built of  $\text{MO}_6$  octahedra and  $(\text{XO}_4)^{n-}$  tetrahedra, for use as positive electrodes in rechargeable lithium batteries [1–4]. Although these compounds have somewhat lower theoretical capacities than simple oxides, the strongly bonded  $(\text{XO}_4)^{n-}$  units confer exceptional stability and safety.  $\text{LiFePO}_4$  has been the most studied, presenting a flat voltage plateau at about 3.4 V versus  $\text{Li}/\text{Li}^+$ , associated with the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple, but it has some kinetic limitations due to the two-phase  $\text{LiFePO}_4/\text{FePO}_4$  system and the limited electronic conductivity of both phases. Significant improvements in rate capability have been achieved by coat-

ing the oxide particles with carbon by physical or chemical means [5,6] and by decreasing the particle size [7]. Hydrated iron phosphates and their dehydrated derivatives [8,9] have generated some interest, but these compounds, too, require carbon coating to overcome their poor electronic conductivity. Materials with composition  $[\text{Li},\text{Na}]_2[\text{Fe},\text{Mn}]_3(\text{PO}_4)_3$ , having the alluaudite structure, were found to remain single-phase during Li insertion, but exhibited poor capacities [10]. Here we report the structural and electrochemical characteristics of the hydrated iron phosphate fluoride  $\text{Fe}_{1.19}\text{PO}_4\text{F}_{0.11}(\text{OH})_{0.46}(\text{H}_2\text{O})_{0.43}$ , having the structure of lipscombite ( $\text{Fe}_{1.5}\text{PO}_4\text{OH}$ ) [11]. In this material (Fig. 1), slightly distorted  $\text{FeO}_6$  octahedra share faces to form chains that are connected to other chains by corner sharing. These structural features could enhance the compound's electronic conductivity relative to that of the highly insulating olivine,  $\text{LiFePO}_4$ , in which  $\text{FeO}_6$  units share only corners. Moreover, if Li intercalation proceeds via a single-phase in which a mixture of iron oxidation states is present, the conductivity may be greater,

\* Corresponding author. Tel.: +1 510 486 8619; fax: +1 510 486 8619.  
E-mail address: [tjrichardson@lbl.gov](mailto:tjrichardson@lbl.gov) (T.J. Richardson).

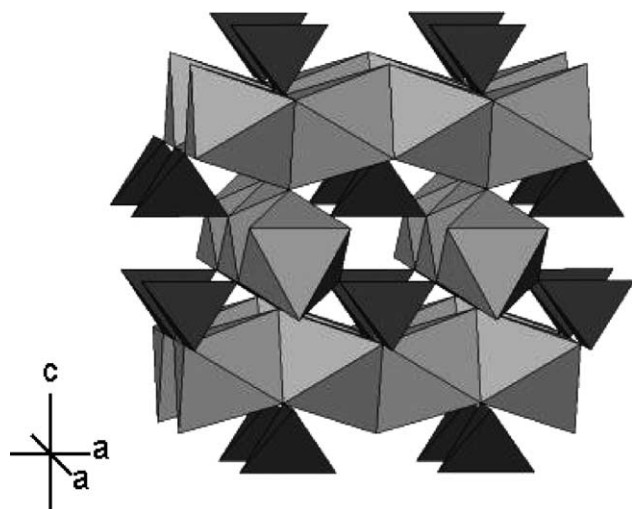


Fig. 1. Structure of  $\text{Fe}_{1.19}\text{PO}_4\text{F}_{0.11}(\text{OH})_{0.46}(\text{H}_2\text{O})_{0.43}$  showing  $\text{FeO}_6$  octahedra (grey) and  $\text{PO}_4$  tetrahedra (black).

and the activation energy for rearrangement of the structure may be lower. As prepared, all iron atoms in  $\text{Fe}_{1.19}\text{PO}_4\text{F}_{0.11}(\text{OH})_{0.46}(\text{H}_2\text{O})_{0.43}$  are in the oxidized (+3, high spin) state, leading to a theoretical capacity of  $180 \text{ mAh g}^{-1}$  if all iron atoms can be reduced and sufficient sites for Li insertion are available. Here we discuss the electrochemical performance of this material in lithium cells and the structural changes observed during cycling.

## 2. Experimental

The synthesis was carried out hydrothermally as reported by Loiseau et al. [11]. A mixture of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{NH}_4\text{HF}_2$ , and  $\text{H}_2\text{O}$  in the molar ratio 1:1:1:40 was held at  $200^\circ\text{C}$  for 6 days in a 60 ml Teflon-lined stainless steel reactor (Parr Co., Moline, IL). The resulting pale brown powder was washed several times with distilled water and dried at room temperature. The sample consisted of well-formed cubo-octahedral crystallites (Fig. 2) about  $5 \mu\text{m}$  in size. XRD patterns were obtained using a Siemens D500 diffractometer with monochromatic  $\text{Cu K}\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The programs FULLPROF [12] and RIQAS (MDI Inc., Livermore, CA) were used for Rietveld refinement by whole pattern fitting. The XRD pattern (Fig. 3) showed it to be single-phase with  $a = 5.181(1) \text{ \AA}$  and  $c = 13.020(8) \text{ \AA}$ , in good agreement with Ref. [11]. Elemental composition was determined by inductively coupled plasma (ICP) atomic absorption analysis (Luvak Inc., Boylston, MA).

$\text{Ti}_5\text{O}_4(\text{PO}_4)_4$  was prepared as follows: titanium isopropoxide was mixed with an excess of  $1 \text{ M H}_3\text{PO}_4$ , producing a white precipitate which was first dried at  $60^\circ\text{C}$  and then heated at  $900^\circ\text{C}$  for 12 h. The resulting white powder was characterized by XRD as  $\text{Ti}_5\text{O}_4(\text{PO}_4)_4$  with a small  $\text{TiP}_2\text{O}_7$  impurity. Rietveld refinement in the  $P2_12_12_1$  space group gave  $a = 12.804(2) \text{ \AA}$ ,  $b = 14.426(3) \text{ \AA}$  and  $c = 7.479(2) \text{ \AA}$ , in

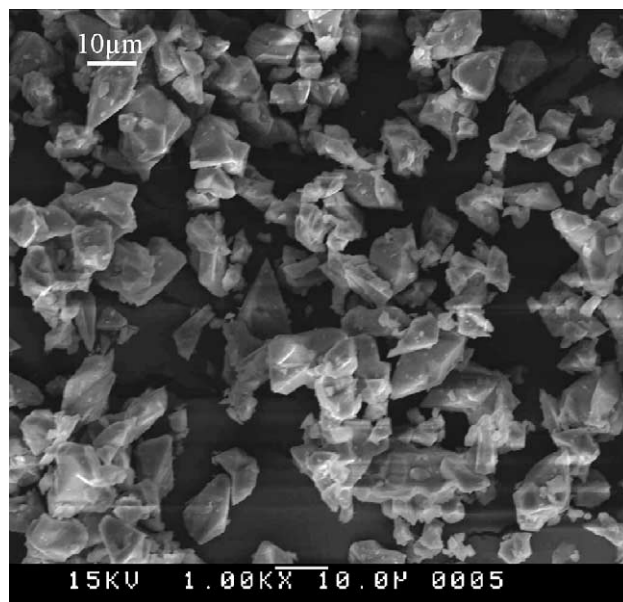


Fig. 2. Scanning electron micrograph of  $\text{Fe}_{1.19}\text{PO}_4\text{F}_{0.11}(\text{OH})_{0.46}(\text{H}_2\text{O})_{0.43}$  particles.

good agreement with those reported from single crystal data [13].

Electrodes were prepared by thoroughly mixing the well-ground phosphates (70.4 wt.%) with 12.4 wt.% carbon black (Shawinigan black) and 17.2 wt.% poly(vinylidenedifluoride) in a 6 wt.% NMP solution. The mixture was applied to aluminum foil by the doctor blade method. The electrodes were dried overnight at ambient temperature and then for 12 h at  $60^\circ\text{C}$  in vacuum. Coin cells were assembled in an argon-filled glove box using Celgard 3401 separators,  $\text{LiPF}_6$  (1 M) in ethylene

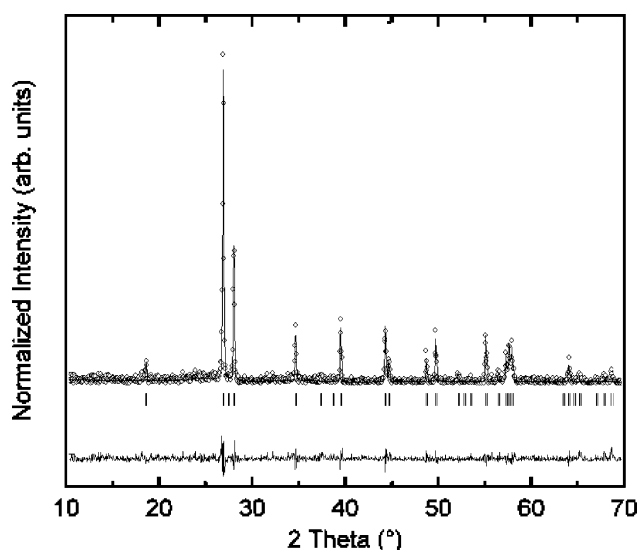


Fig. 3. XRD pattern refinement of  $\text{Fe}_{1.19}\text{PO}_4\text{F}_{0.11}(\text{OH})_{0.46}(\text{H}_2\text{O})_{0.43}$ : open circles represent experimental data points, upper solid line denotes calculated pattern, lower solid line represents the difference, vertical bars indicate the locations of reflections.

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