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30 Oxidative decomposition products of synthetic NaFePO₄
31 marićite: nano-textural and electrochemical characterization

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44 **Abstract**

45 Single-phase marićite, NaFePO₄, was synthesized from monosodium phosphate and
46 iron oxalate at 750°C, at atmospheric pressure. Thermal treatment of synthetic marićite in air
47 indicated oxidative decomposition into Na₃Fe³⁺₂(PO₄)₃ nasicon and α-Fe₂O₃ at temperatures
48 above 225°C. Intergrowth of the reaction products is found to occur at the nanoscale without
49 identified crystallographic relationship with the marićite precursor. Electrochemical activity of
50 the reaction product is confirmed with the reversible insertion of one Na at 2.55 V vs Na⁺/Na⁰.

51 **Keywords:** sodium iron phosphate; marićite; sodium-ion batteries; oxidative decomposition;
52 NASICON

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55 **Introduction**

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57 The phosphatic iron formation of the Big Fish River area (Yukon Territory, Canada) has
58 revealed a remarkable number of new phosphate occurrences (*e.g.*, Mandarino & Sturman,
59 1976; Sturman & Mandarino, 1976; Robertson, 1982; Tait *et al.*, 2011) among which, lazulite
60 is probably the most famous (Campbell, 1962). The sodium iron phosphate, marićite, ideally
61 NaFePO_4 , was also discovered in the Big Fish River area in interbedded shales and sideritic
62 ironstone where it can be found as monomineralic nodules within the shale beds (Sturman *et*
63 *al.*, 1977). Marićite was named in honor of Prof. Dr. Luka Marić and should therefore be written
64 with a “ć” although the acute accent is often dropped in the literature. Marićite has also been
65 described in iron meteorites (*e.g.*, Olsen *et al.*, 1999). Its crystal structure was solved on a
66 Yukon Territory specimen of composition $\text{Na}_{1.0}(\text{Fe}_{0.9}\text{Mn}_{0.6}\text{Mg}_{0.3}\text{Ca}_{0.1})\text{PO}_4$ in the Pnmb space
67 group (Le Page & Donnay, 1977). In addition to its mineralogical interest, marićite is also
68 known as a common corrosion product of power plant boiler (Cole *et al.*, 1997). It is however
69 in the electrochemistry community that marićite is probably the most popular. Indeed, marićite
70 may turn out, through its polymorphism, to be a promising compound for the manufacture of
71 the positive electrode of sodium ion batteries. With a high energy-density and enhanced rate
72 capabilities (Etacheri *et al.*, 2011), Li-ion batteries have been developed to meet the technical
73 constraints of mobile applications. However, critical issues have been identified in the lithium
74 supply chain which raised concern about the ability of the Li resource to meet the demand of
75 the fast-growing Li-battery market. In particular, geographical concentration of the Li resource
76 and a trade that is highly dependent on geopolitical issues have been pointed out (*e.g.*, Egbue
77 & Long, 2012). This economic situation has fostered research to substitute lithium by more
78 abundant elements such as sodium. Indeed, one could potentially take advantage of isomorphic

Na - Li substitutions which lead to close electrochemical properties for the manufacture of sodium ion batteries (Meethong *et al.*, 2007; Chiang *et al.*, 2012). A key challenge for sodium ion batteries turned out to be the stabilization of NaFePO₄ olivine (NFP) since conventional direct synthesis of NFP leads to the formation of marićite which is of poor electrochemical interest (*e.g.*, Kosova *et al.*, 2014). Indeed, the synthesis of olivine NFP requires an electrochemical step with the intercalation of Na in FePO₄-olivine or the replacement of Li by Na in LiFePO₄ (Moreau *et al.*, 2010).

Unexpectedly, Kim *et al.* (2015) reported on an electrochemically active marićite resulting from the formation of amorphous FePO₄ after the first charge. This result stimulated a revival of interest for marićite as a promising low-cost material for sodium ion batteries.

In order to further evaluate the potential of marićite for electrochemical applications, we investigated its thermal stability in air at moderate temperature. Indeed, thermal stability is one of key parameters for battery materials. Furthermore, oxidative decomposition of ferrous compounds may produce electrochemically active compounds due the formation of Fe vacancies. This is typically the case for silicates and phosphates with an olivine-related structure for which oxidation in air triggers a process of iron expulsion accompanied by the formation of Fe₂O₃ oxide particles with preservation of the original crystallographic structure of the starting iron phosphate or silicate. For example, thermal oxidation under air at moderate temperature of synthetic LiFe²⁺PO₄ lithiophilite leads to the formation of an isostructural LiFe³⁺_{2/3}PO₄ compound with the partial exsolution of iron in the form of nanosized Fe₂O₃ particles (Hamelet *et al.*, 2011). Similar process has been described with Fe₂SiO₄, fayalite, which transforms upon heating in air into a structurally defective Fe³⁺-bearing olivine group silicate, laihunite (Kondoh *et al.*, 1985). Similarly, Crouzet *et al.*, (2016) have showed that heating in air of synthetic sarcopside, Fe²⁺₃PO₄, which also writes (Fe²⁺_{3/2}, □_{1/2})₂PO₄ in order to emphasize its olivine-related structure, leads to the formation of Fe³⁺PO₄ along with Fe₂O₃ nanoparticles; Fe³⁺PO₄

displays an heterosite structure which is also based on an olivine atomic arrangement (Eventoff *et al.*, 1972).

Based on the above examples, it can be anticipated that NaFePO₄ marićite should transform into NaFe_{2/3}PO₄ + Fe₂O₃ upon heating in air. The determination of both the crystal structure of the possible NaFe_{2/3}PO₄ phase and its electrochemical properties have been the main incentive of this work.

Material and methods

Methods

A starting material of marićite stoichiometry was prepared by milling monosodium phosphate, NaH₂PO₄, and iron oxalate, FeC₂O₄.2H₂O, with a SPEX 8000 ball mill for 20 mn. Marićite was successfully synthesized by reacting the starting material in a tubular furnace at 750 °C for 48 hours under an argon gas flow as follows:

The reaction products were then crushed and submitted to gradual heating from 150°C to 600°C following 75°C heating steps. After 12 hours at each isothermal step, X-ray powder diffraction patterns were collected ex-situ at room temperature.

Solid characterization

X-Ray Powder Diffraction (XRPD) was conducted on solid samples before and after thermal treatment with a Bruker D8 diffractometer (CuK α radiation). Space groups and reported lattice parameters were retrieved from peak indexation and Rietveld refinement using JANA2006 software¹³. Thermal behavior and stability of marićite was analyzed by Thermal Gravimetric Analysis (TGA, STA 449C Jupiter unit, Netzsch Inc). A 10 °C / min heating ramp was applied from 25 to 700 °C. Electron microscopy imaging was performed using a Scanning Electron

Microscope (SEM, Quanta 200 ESEM FEG FEI) in secondary electron mode. Powder samples were mounted on a double-sided carbon tape and carbon coated. Decomposition textures were characterized at the nano-scale using transmission electron microscopy (TEM) analysis with a Tecnai F20 S-TWIN FEI. An automated crystal orientation and phase mapping in TEM (ASTAR, Rauch & Véron, 2014) was realized to unravel textural relationships at the nanoscale. The corresponding images were generated by plotting the intensity of the transmitted electron beam in the series of acquisition. An intensity of minimum 42 has been chosen in order to eliminate the points that presented a low reliability. This method of investigation has been already used for the study of different materials as thin films (Izadi *et al.*, 2017; Wang *et al.*, 2012), alloys (Rauch *et al.*, 2012) and batteries (Norby *et al.*, 2016). A region of interest of $1.2 \mu\text{m}^2$ was chosen for the scanning area with a step size of 5 nm. A precession semi-angle (Nicolopoulos & Bultreys, 2012) of 0.5° was used in order to reduce the dynamical effects and increase the quality of the electron diffraction pattern.

Results

Marićite synthesis and oxidative decomposition in air

XRPD investigation indicated successful synthesis of single-phase marićite, NaFePO_4 (Figure 1). Marićite lattice parameters were retrieved from Rietveld refinement using the Pmna space group, $a = 6.8648(3) \text{ \AA}$, $b = 8.9795(4) \text{ \AA}$ and $c = 5.0420(2) \text{ \AA}$ ($R = 4.32\%$, $R_p = 0.53$ and $\text{GOF} = 1.65$). They are consistent with the lattice parameters published by Le Page & Donnay (1977). The marićite product is composed of euhedral elongated grains up $150 \mu\text{m}$ long (Figure 1b). The XRPD patterns of synthetic marićite submitted to stepwise heating until 600°C in air are summarized in Figure 2a. The onset of oxidative decomposition of marićite occurs between 225°C and 300°C since newly formed $\text{Na}_3\text{Fe}^{3+}_2(\text{PO}_4)_3$ and hematite (Fe_2O_3) diffraction peaks are visible on the 300°C diffraction pattern. Above 375°C , full marićite decomposition is

achieved and no further change is observed in powder diffraction patterns collected above this temperature and up to 600°C. Profile matching was performed on the XRPD diffractogram of the solid sample recovered after the last heating step at 600 °C (Figure 3). Space groups and structural parameters of Na₃Fe₂(PO₄)₃ were defined as C_{2/c} with a = 15.084(2) Å, b = 8.7860(2) Å, c = 8.7828(2) Å and β = 124.760(8)°, (Rp = 0.49 and GOF = 1.54), in accordance with reported literature for NASICON-type α-Na₃Fe₂(PO₄)₃ (Kabbour *et al.*, 2011).

Thermal behavior of mariçite was also investigated by TGA in air (Figure 2b). A mass gain related to iron oxidation was observed from 275 °C to 600 °C with a rate which occurred to be maximum at the beginning of the mariçite breakdown and minimum at around 350 °C. Heating rates and temperature resolution strongly differ between TGA and XRPD monitoring through step heating. Considering these experimental differences, the temperatures of 225 and 275 °C found using TGA and XRPD, respectively, are likely to characterize the same process, *i.e.*, the onset of maricite oxidative decomposition. Total mass gain derived from TGA (4.53%) is close to the expected value of 4.6 %_w for the full conversion of NaFePO₄ into Na₃Fe₂(PO₄)₃ according to the following reaction:

was observed in two range of particle sizes with flat particles around 5 – 20 µm long and large ones around 100 – 200 µm long (Figure 3b).

FE-SEM microscopy showed that synthetic mariçite crystallized into elongated prisms with lengths centered around 5 – 20 µm and 100 – 200 µm (Figure 1a). FE-SEM images obtained on the products of mariçite decomposition in air, also show elongated grains of similar size covered with nanoparticles (Figure 3b). The combination of XRPD and FE-SEM EDS data suggest that Figure 3b can be interpreted as nanoparticles of hematite covering pseudomorphic Na₃Fe₂(PO₄)₃ grains after mariçite.

A phase recognition image was realized on partially decomposed marićite by comparing electron diffraction pattern in every point with all the orientation possible for every structure. A phase map image (Figure 4) shows the intimate intergrowth of α -Fe₂O₃ (trigonal, $a=5.038$ Å and $c=13.770$ Å) and Na₃Fe₂(PO₄)₃ (trigonal, $a=8.72$ Å and $c=21.80$ Å) within residual NaFePO₄ (Pnma, $a=9.01$ Å, $b=6.87$ Å, $c=5.05$ Å). Figure 4e,f,g displays the electron diffraction pattern chosen randomly in the specimen for α -Fe₂O₃, NaFePO₄, and Na₃Fe₂(PO₄)₃. No preferred crystallographic orientation could be evidenced among the marićite decomposition products (Fig S1). Reaction (2) could be reversed at 450°C under an Ar / 10% H₂ mixture, marićite was recovered along with a minor compound that could not be index using X-ray diffraction (Fig. S2).

Sodium insertion

Reversible sodium insertion cycles were performed on $\text{Na}_3\text{Fe}^{3+}_2(\text{PO}_4)_3 + \text{Fe}_2\text{O}_3$ samples obtained from thermal oxidation of marićite. The first discharge and charge step is plotted in Figure 5 and shows a plateau centered at 2.55 V vs Na^+/Na^0 as confirmed by dx/dV curve displayed in Fig.5. At maximum of reduction, due to structural stress, only one Na is inserted in the lattice to reach $\text{Na}_3\text{Fe}^{2+}\text{Fe}^{3+}(\text{PO}_4)_3$ composition. Sodium disinsertion is then total and occurs with a very low polarization which can be attributed to the porosity created during the iron (II) output from the structure which can enhanced ionic conduction by a good electrolyte percolation in the electrode. The electrochemical performances of marićite have been tested under experimental conditions close to those described in Kim *et al.* (2015). Marićite product was either grinded down to amorphization with a SPEX800 mill or treated in air from room temperature to 250°C for 12 hours. However, none of these treatments improved marićite electrochemical performances since in all electrochemical tests, the measured capacity did not exceed 20 % of the theoretical capacity (155 mA.h.g⁻¹).

Discussion

The poor electrochemical properties of marićite as Na-ion positive electrode measured in this study are consistent with previous studies. The absence of sodium mobility has been explained on crystallographic grounds due to the absence of cationic diffusion channel in the marićite structure leading to Na^+ entrapment (Ellis *et al.*, 2007; Palomares *et al.*, 2012). Despite grinding and mild heating, sodium mobility described in marićite by Kim *et al.* (2015) could not be achieved here. The electrochemical activity of maricite formed after thermal reduction of its oxidation product, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3 + \text{Fe}_2\text{O}_3$, has not been tested.

The monitoring of marićite transformation upon heating in air using both ex-situ powder XRD and ATG shows that synthetic NaFePO_4 decomposes into $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3 + \text{Fe}_2\text{O}_3$ at a temperature comprised between 225 and 300 °C. Both X-ray and electron diffractions indicate that $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ crystallizes into a NASICON-type structure with Fe being trivalent. Overall, the thermal treatment of marićite in air leads to the oxidation of iron which is expelled from the marićite structure and crystallizes in the form of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles. The formation of hematite nanoparticles coating onto the surface of an iron phosphate under mild temperature conditions in air has already been described in the literature for barium phosphates (*e.g.*, David *et al.*, 2014; Blazquez-Alcover *et al.*, 2015). Iron expulsion and oxidation is found to occur through an isomorphic process where $\text{BaFe}_{2-x}(\text{PO}_4)_2$ partially to fully oxidized $\text{BaFe}_{2-x}(\text{PO}_4)_2$ phases (with $0 < x < 2/3$). Similarly, Crouzet *et al.* (2016) reported on the covering of FePO_4 with Fe_2O_3 nanoparticles after $\text{Fe}_3(\text{PO}_4)_2$ sarcopside oxidation in air. Again, oxidation reaction follows an isomorphic process where iron is expelled and oxidized and where the initial crystallographic structure of the phosphate remains unchanged during the process. Here, a detailed nano-textural study of the decomposition products shows that although precursor and products share crystallographic relationships, $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ and NaFePO_4 marićite have distinct crystallographic structures. The exsolution of iron oxide does not therefore proceed in conjunction with the isomorphic oxidation of the precursor mineral as described for olivine-structure phosphates and barium phosphates. Oxidation in air at mild temperatures leads to a coupled reaction-transport mechanism where oxidative decomposition creates new pathways for O_2 transport (new grain boundaries). The resulting nano-scale mixing of the reaction products observed using TEM (Fig.4d) may enhance ionic conductivity through the high-density of grain boundaries (and possibly pores) which act as diffusive paths for sodium disinsertion - insertion cycles translates by lower polarization were observed.

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Figures

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377 **Figure 1:** (a) Rietveld refinement of the synthetic maričite used as starting material for a thermal
378 treatment. (b) FE-SEM imaging in secondary electron mode before oxidation of maričite in air
379 at 600°C

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Figure 2: Characterization of the marićite thermal behavior in air; (a) Thermal gravimetry analysis in the 25 – 700 °C range using a heating ramp of 10 °C / min. (b) ex-situ diffractograms after stepwise heating of 12 h in the 30 – 600 °C range.

Figure 3: (a) XRPD profile matching of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3 + \text{Fe}_2\text{O}_3$ obtained after thermal decomposition of synthetic mariçite. (b) FE-SEM imaging in secondary electron mode before oxidation of synthetic mariçite in air at 600 °C.

Figure 4: (a) TEM image of pristine NaFePO₄ crystal, (b) SAED pattern of NaFePO₄ single-crystal aligned along the [010] direction of the *Pnma* structure. (c) Virtual bright field image based on transmitted electron beam in the ASTAR series acquisition of crystal after annealing process. The dark area from the phase map image correspond to areas where the sample is too thick. (d) Phase mapping based on treatment electron diffraction mapping acquired in precession method. (e,f,g) electron diffraction pattern acquired using ASTAR system for α-Fe₂O₃, NaFePO₄, and Na₃Fe₂(PO₄)₃ respectively along the directions [001], [100] and [001].

Figure 5: Electrochemical performances versus Na^+/Na^0 of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$: potential versus composition curves obtained from sample synthesized after thermal oxidation of maricite NaFePO_4 in air. The derivative curve (dx/dV) is plotted as function of electrochemical potential in the insert.

Supplementary material

Figure S1: TEM analysis based on acquisition series of local electron diffraction patterns using precession mode (Astar system) (a) Orientation map according to Z axis in which no preferential orientation is observed and (b) phase mapping in which α -Fe₂O₃ is red, NaFePO₄ is green, and Na₃Fe₂(PO₄)₃ is blue.

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439 **Figure S2:** Comparison of XRPD patterns of initial synthetic maricite (bottom, black) and
440 maricite formed after reverse transformation of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3 + \text{Fe}_2\text{O}_3$ biphasic product (top,
441 red) at 450 °C for 48 hours under 10 % H_2 – 90 % Ar atmosphere; additional and unidentified
442 peaks are indexed with a star (*).

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