Low temperature treatment and structural characterization of Na$_2$M$_2$Fe(PO$_4$)$_3$ (M= Mn or Ni) Alluaudite phases

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Abstract. Materials for sodium intercalation were recently considered as attractive potential cathode materials for Na-ion Batteries. Amongst others, Alluaudite phases have shown interesting electrochemical properties. Thanks to their structure which consists of a three-dimensional framework of octahedra and tetrahedra sharing corners and/or edges, giving rise to two types of 1D tunnels where the Na$^+$ ions can be intercalated. As first attempt to optimize the electrochemical performances of two alluaudates phases used as cathode materials, namely, Na$_2$Mn$_2$Fe(PO$_4$)$_3$ and Na$_2$Ni$_2$Fe(PO$_4$)$_3$, we have prepared these compounds by co-precipitation method with controlled nanometric size and low calcination temperature of 700°C and 750°C respectively. The structure of both samples obtained at different calcination temperatures were investigated using powder X-ray diffraction. The experimental results show the purity of Na$_2$Mn$_2$Fe(PO$_4$)$_3$ and Na$_2$Ni$_2$Fe(PO$_4$)$_3$ phases as well as the high crystallinity while maintaining low particle size and low calcination temperatures, namely less than 100 – 150°C difference.

1. Introduction

Energy and climate concerns have made the need for research towards electrical energy storage. In this context, sodium ion battery (SIBs) has attracted significant attention thanks to its huge availability, its low price and the similarity of both Li and Na insertion chemistries which makes the transition into using Na chemistry for ion battery systems feasible [1]. In spite of the lower energy density and voltage of Na-ion based technologies, they can be focused on applications where the weight and footprint requirement is less drastic, such as electrical grid storage that integrates discontinuous energy flow from renewable sources, optimizing the performance of clean energy sources [2]. In this regard much work has to be done in the field of Na-ion, cathodic and anodic materials must be optimized to find electrochemical couples that are suitable in terms of capacity and cycle life for NaIBs.

Thus, since the discovery of highly interesting properties of olivine phase LiFePO$_4$ as a positive electrode material, several polyphosphate based compounds have been extensively studied as electro-positive materials in Na-ion batteries [3]. Among the large number of existing sodium phosphate phases, the alluaudite-type compounds have been extensively studied; thus, different research groups have recently reported diverse alluaudite compounds containing di and/or trivalent metals, with a monoclinic symmetry and C2/c space group [4][5], or an orthorhombic crystal structure with Imma
space group with a more symmetric polyanionic framework.[6][7]

It is worth to mention that the alluaudite structure was first determined on natural minerals by Fisher[8], who showed that alluaudite compounds crystallize in the monoclinic C2/c space group. Whereas the general formula X(2)X(1)M(1)M(2)2(PO4)3, was proposed by Moore [9]in which X and M cations are written according to decreasing size. where its structure consists of a three-dimensional framework made up of infinite chains formed by a succession of octahedral M(2) pairs connected by highly deformed M(1) octahedra sharing edges, and the equivalent chains are connected by phosphate tetrahedra to form sheets oriented perpendicular to [010] than equivalent sheets are held together as well by PO4 tetrahedra to form a three-dimensional architecture with two sets of tunnels in the c direction: tunnel 1 (1/2, 0, z) and tunnel 2 (0, 0, z) where X1 and X2 are cations residing in different sites of these tunnels.

The electrochemical performances are strongly affected by the synthesis condition for the sake of difference in homogeneity and for their dependency on the size and the morphology of the particles [10][11]. Therefore, the control of homogeneity and integrity of the host structure are most important factors to obtain better electrochemical properties such as high reversible capacity and stable cycling performance. In this paper, we report on the synthesis and characterization of Na2Mn2Fe(PO4)3 and Na2Ni2Fe(PO4)3 prepared by co-precipitation method, and calcinated at different high temperatures. As compared to literature, the co-precipitation method allowed us to reduce the calcination temperature by up to 150°C while maintaining very low nanometric particle size and good crystallinity. [12]

2. Experimental Section

2.1 Synthesis

Both samples of Na2Mn2Fe(PO4)3 and Na2Ni2Fe(PO4)3, were prepared by the co-precipitation method from mixing appropriate amounts of Na2CO3 (99.5%, Sigma-Aldrich), Fe(NO3)3·9H2O (99%, Sigma-Aldrich) and Mn(CH3CO2)2·4H2O (99%, Sigma-Aldrich) or Ni(CH3CO2)2·4H2O (99%, Sigma-Aldrich) in distilled water under vigorous magnetic stirring, then the required amount of NH4H2PO4 (99%, Panreac - AppliChem) dissolved in distilled water was slowly added to the mixture and stirred for 12h. The excess water was then evaporated by heating at 70°C and the residual powders were ground in an agate mortar then placed in a muffle furnace and heated at 200°C for 24h with a heat rate of 5°C per min, then at 400°C for 24h to get rid of organic chemical compounds and finally calcinated at 600°C, 700°C, 750°C, 800°C and 850°C for 48h. At the end of the synthesis, the powder obtained by final quenching of the product is pale yellow for nickel and brown for manganese compound.

2.2 X-ray diffraction

The X-ray powder diffraction patterns were recorded using a Panalytical diffractometer operating with CuKα radiations at a wavelength of Kα1 = 1.54060 Å and Kα2 = 1.54443 Å, and the data were collected over the 2θ angle range of 10° ≤ 2θ ≤ 80° with a step size of 0.017°.

3. Characterization analysis

3.1 Phase analysis of materials

X-ray powder diffraction was used in this work to identify crystalline phases and to analyze their structures, as shown in Figures 1 and 2. The analysis of X-ray diffraction spectra of the compound Na2Mn2Fe(PO4)3 carried out at different temperatures showed that the compound is pure can be indexed in the monoclinic space group C2/c. Further, as it can be seen from Figure 1, that at higher calcination temperatures, the Bragg peaks become sharper and clearer, indicating that the crystallinity is increasing.
Figure 1. X-ray powder diffraction patterns of Na$_2$Mn$_2$Fe(PO$_4$)$_3$ calcinated at different temperatures.

The inset corresponds to a zoom of the $2\theta = 32$ to 36.6° area.

The particle size of the crystallites was calculated using the Scherrer equation according to the following relation:

$$D = \frac{K\lambda}{\beta \cos(\theta)}$$

Where (D is the size of crystals; K is a dimensionless shape factor, with typical value of about 0.9; $\lambda$ is the X-ray wavelength; $\beta$ is the line broadening at half the maximum intensity (FWHM); $\theta$ is the Bragg angle).

Table 1 and 2 report the measured Full width at half maximum (FWHM) of two intense peaks from the X-ray patterns, as well as the calculated average particles size.

| hkl    | 20 °   | 600°C  | 700°C  | 750°C  | 800°C  | 850°C  |
|--------|--------|--------|--------|--------|--------|--------|
| (-240) | 32.74664 | 0.57017 | 0.20785 | 0.18659 | 0.17629 | 0.1666 |
| (-132) | 35.18682 | 0.65292 | 0.28529 | 0.27127 | 0.24849 | 0.25319 |

Thus we can notice from table 1 and figure 3 that, with the increase of the calcination temperature, the width of diffraction peaks is lowered, while the average size increase in the range between 136 and 413 nm. This clearly indicates that the high temperature calcination induce a rise in the agglomeration of the powder and an increase in the average particle size. Hence we opted for a calcination at 700°C due to the good crystallinity of the powder, and a relatively small particle size. Whereas its analogue was synthesized by a solid-state reaction carried out in air and progressively heated to 850°C, in order to obtain high-purity alluaudite [13]. In that the possibility of improving their performance through particle size reduction is being investigated, owing to important role that plays this latter in the electrochemical performances.[10]
Similarly, the investigation of the diffractogram of the Na$_2$Ni$_2$Fe(PO$_4$)$_3$ phase indicates that this compound crystallizes in the orthorhombic structure with the space group Imma, which is in concordance with previous work [14]. As for the manganese counterpart, the choice of the optimum temperature, the influence of crystallinity and of agglomeration factors have been taken into account exhaustively, and as it can be seen from Figure 2, the characteristic diffraction peaks of the different spectra corresponding to calcination temperatures ranging from 600°C to 850°C, exhibit a slight difference namely, in crystallinity. Therefore, Na$_2$Ni$_2$Fe(PO$_4$)$_3$ powder calcined at 750°C was chosen, where the low intensity peaks appear more clearly in the spectrum of 700°C with high crystallinity, and rather lower than the high temperature of 850°C required for the synthesis by solid state reaction [14]. Ultimately, a decrease of full width at half maximum (FWHM) of the peaks as the temperature rises was noticed (Table 2) therefore we estimate through the widths measured and by using the Scherrer formula, an average size ranging between 177 and 463 nm (Figure 3), confirming that the higher temperature certainly lead to more severe powder agglomeration.[15]

![Figure 2. X-ray powder diffraction patterns of Na$_2$Ni$_2$Fe(PO$_4$)$_3$ calcinated at different temperatures. The inset corresponds to a zoom of the 2θ = 31.5 to 34.8° area.](image)

| hkl | $\theta$ (°) | 600°C | 700°C | 750°C | 800°C | 850°C |
|-----|-------------|-------|-------|-------|-------|-------|
| -400 | 34.4061 | 0.65691 | 0.22961 | 0.17766 | 0.18418 | 0.1597 |
| -251 | 40.75677 | 0.34147 | 0.2954 | 0.22598 | 0.22361 | 0.18513 |
| $D_{avg}$ (nm) | | 177.0117 | 307.8440 | 399.8518 | 393.7924 | 463.861 |

Table 2. Full width at half maximum (FWHM) of (400) and (251) peaks
Figure 3. The average size crystals of Na$_2$Mn$_2$Fe(PO$_4$)$_3$ and Na$_2$Ni$_2$Fe(PO$_4$)$_3$ samples calcinated at different temperatures.

3.2 Structure refinement
The unit-cell parameters and the atomic positions reported for Na$_2$Mn$_2$Fe(PO$_4$)$_3$, and for Na$_2$Ni$_2$Fe(PO$_4$)$_3$ have served as the starting parameters for the Rietveld refinement of the synthesised compounds which were performed with Fullprof program [13] [14]. The Rietveld refinement plot of the two synthesised phases is shown in Figure 4 and the refined cell parameters are listed in Table 3.

Table 3. Crystallographic and structure refinements data

| Rietveld Refinement | Na$_2$Mn$_2$Fe(PO$_4$)$_3$ | Na$_2$Ni$_2$Fe(PO$_4$)$_3$ |
|---------------------|-----------------------------|-----------------------------|
| Structural formula  | Na$_2$Mn$_2$Fe(PO$_4$)$_3$  | Na$_2$Ni$_2$Fe(PO$_4$)$_3$  |
| Molecular weight    | 496.61                      | 504.11                      |
| Crystal system      | Monoclinic                  | Orthorhombic                |
| Space group         | C2/c (No 15)                | Imma (No 74)                |
| Cell dimension (Å)  | a=12.0311(13)               | a=10.4063(17)               |
|                     | b=12.6122(14)               | b=13.195(2)                 |
|                     | c=6.4972(6)                 | c=6.4882(11)                |
|                     | β=114.492(7)                | β = α = γ = 90°             |
| Cell volume (Å$^3$) | 897.16(16)                  | 890.9(3)                    |
| Z                   | 2                           | 4                           |
| goodness of fit χ2  | 0.7745                      | 1.04                        |
| Agreeing factors    | Rp  = 49.2                  | Rp  = 36.2                  |
|                     | Rwp = 33.1                  | Rwp = 22.5                  |
|                     | Rexp = 37.6                 | Rexp = 22.02                |
| No. of parameters   | 56                          | 37                          |
| Profile function    | Pseudo-Voigt                |                             |
| Background          | 6-coefficients polynominal  |                             |
One can notice from the Rietveld refinement of Na$_2$Mn$_2$Fe(PO$_4$)$_3$ and Na$_2$Ni$_2$Fe(PO$_4$)$_3$ compounds (Figure 4) that the refinement converges towards a good agreement between the experimental and calculated diffractograms, which confirms the adequacy of the structural model.
From the Rietveld analysis the bond distance analysis for Na-O, Fe-O, Ni-O and Mn-O gives rather satisfactory results, in agreement with the theoretical values as calculated from Shannon ionic radii table [16] (see Tables 4 and 5).

Table 4. Selected interatomic distances (Å) determined for Na$_2$Mn$_2$Fe(PO$_4$)$_3$ from the Rietveld Refinement of the XRD data.

| Distance          | Value    |
|-------------------|----------|
| Na(2)' - O(1)     | 3.27(5)  |
| Na(2)' - O(1)     | 1.36(5)  |
| Na(2)' - O(2)     | 2.42(4)  |
| Na(2)' - O(3)     | 2.19(5)  |
| Na(2)' - O(3)     | 2.59(4)  |
| Na(2)' - O(4)     | 2.67(3)  |
| Na(2)' - O(4)     | 2.56(4)  |
| Na(2)' - O(5)     | 3.27(3)  |
| <Na(2)' - O>      | 2.54     |
| Mn(1) - O(2)      | 2.54(3)  |
| Mn(1) - O(2)      | 2.54(3)  |
| Mn(1) - O(3)      | 1.66(3)  |
| Mn(1) - O(4)      | 2.62(2)  |
| P(1) - O(1)       | 1.52(4)  |
| P(1) - O(2)       | 1.63(5)  |
| P(1) - O          | 1.57     |

Table 5. Selected interatomic distances (Å) determined for Na$_2$Ni$_2$Fe(PO$_4$)$_3$ from the Rietveld Refinement of the XRD data.

| Distance          | Value    |
|-------------------|----------|
| Na(1) - O(1)      | 2.664(9) |
| Na(1) - O(4)      | 2.747(7) |
| Na(1) - O(3)      | 2.587(6) |
| <Na(1) - O>       | 2.666    |
| Ni(1)/Fe(1) - O(1) | 2.106(3) |
| Ni(1)/Fe(1) - O(2) | 2.073(5) |
| Ni(1)/Fe(1) - O(4) | 2.047(9) |
| Ni(2)/Fe(2) - O(2) | 2.006(4) |
| Ni(2)/Fe(2) - O(3) | 2.025(6) |
| Ni(2)/Fe(2) - O   | 2.015    |
| P(1) - O(1)       | 1.522(4) |
| P(1) - O(2)       | 1.552(9) |
| P(1) - O          | 1.537    |
| <P(1) - O>        | 1.541    |

3.3 Crystal structure

The following polyhedral representation (Figure 5) illustrates a projection view of the crystal structure of the title phase along (a) and (b) directions. Where we notice very well that the structure is formed by a linear sequence of MnO$_6$ octahedron with FeO$_6$ octahedra, forming a tri-dimensionnel structure mainly by phosphate tetrahedra and thus giving rise to cavities in the c direction where the sodium ions are inserted.
The orthorhombic structure (Figure 6) of the nickel compound can be easily described by considering the association of two anionic building entities, the first entity composed of infinite chains parallel to the \( \mathbf{b} \) axis, obtained by the iron octahedra \( \text{FeO}_6 \) and the tetrahedra of phosphate. While the second entity formed by the association of two Nickel octahedral dimers sharing edges with phosphate tetrahedra. Consequently, these entities share the corners of oxygen with the adjacent units to form an infinite layer, associated in its turn to form a three-dimensional anionic frame with the creation of two channels along the directions \( \mathbf{a} \) and \( \mathbf{b} \), occupied by the \( \text{Na}^+ \) cations as shown in the crystal structure.

Figure 5. Projections of the monoclinic structure of \( \text{Na}_2\text{Mn}_2\text{Fe}(\text{PO}_4)_3 \) along the \( \mathbf{c} \) axis.

Figure 6. Projections of the crystal structure of \( \text{Na}_2\text{Ni}_2\text{Fe}(\text{PO}_4)_3 \) along the \( \mathbf{c} \) axis.
Conclusion
Two Alluaudite phases Na$_2$M$_2$Fe(PO$_4$)$_3$ with (M=Mn, Ni) were prepared by co-precipitation method, and the Rietveld refinement of their XRD data indicate that these phases crystallised in the monoclinic system for manganese and orthorhombic for nickel compounds. The powders at different calcination temperatures were characterized by XRD analysis and then compared by considering the crystallinity and the effect of high temperature on the size of crystallites, as a smaller grain size is favorable to the sodium intercalation process in the primary particles by reducing the length of the ionic diffusion path. Na$_2$Mn$_2$Fe(PO$_4$)$_3$ calcinated at 700°C and Na$_2$Ni$_2$Fe(PO$_4$)$_3$ calcinated at 750°C were selected as optimum temperatures to explore their effectiveness as cathode materials for Na-ion battery.

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