



# Facile solvothermal synthesis of $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ : Electrochemical study as a dual electrode material for lithium-ion batteries

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## ABSTRACT

$\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  (where  $\square$  denotes vacancies) microrods were obtained through a solvothermal synthesis in ethylene glycol. The combination of the XRD, Mössbauer and magnetic analyses confirm that the sodium vacancies in the  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  structure are linked to the oxidation of Mn and Fe transition metals. The electrochemical tests have shown that  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  is a dual electrode material for Li-ion batteries. The electrochemical study in the potential range of 1.5–4.5 V indicate that such material can be used as 3 V cathode with specific capacities of 109, 97, and 80  $\text{mAh}\cdot\text{g}^{-1}$  at current densities of 5, 10, and 20  $\text{mA}\cdot\text{g}^{-1}$ , respectively. When it is tested in the potential range of 0.03–3.0 V as negative electrode material, it delivers a reversible capacity of about 170  $\text{mAh}\cdot\text{g}^{-1}$  at 200  $\text{mA}\cdot\text{g}^{-1}$  current density during > 100 cycles.

## 1. Introduction

Iron phosphate-based alluaudite materials have recently attracted increasing attention as promising cathode materials for next-generation lithium-ion batteries (LIBs) and sodium-ion batteries (NIBs), or in hybrid-ion batteries (HIBs) where a sodium-containing pristine cathode material is cycled with a Li-based electrolyte [1–4]. The importance given to this alluaudite group is due to their stability at high temperature, the presence of vacancies allowing easy intercalation of many  $\text{Na}^+/\text{Li}^+$ -ions in their crystal structures, excellent cyclability as well as their environmental friendliness and low cost [3,5,6]. Due to their high molecular weight, phosphate based alluaudites have generally rather low theoretical capacities. However, the existence of vacancies owing to their complementarily and synergetic effect in the insertion/extraction process may enhance their specific capacities and ensures good cycling performances as cathode materials for HIBs, LIBs and NIBs. Due to the low conductivity of iron based phosphate materials, various techniques have been used such as coatings, formation of composites with conducting materials to enhance their conductivity and improve electrochemical performances of these materials in LIBs and NIBs [7–10].

The  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  compound (where  $\square$  denotes vacancies) was previously obtained by F. Hatert et al. by solid state

synthesis route to investigate its crystallographic structure [11,12]. In addition, they proposed this material may be among the promising electrodes for LIBs and NIBs due to the interesting properties presented by the iron phosphate-based alluaudite materials as detailed above. However, the solid state synthesis offers less morphology and composition control than wet chemistry approaches [13–15].

In the recent years, a large number of solvothermal syntheses have emerged for iron-phosphate materials [16–20] that offer many advantages such as low temperature processes, fast reaction kinetics, short processing times, phase purity, high crystallinity, high yield, homogeneous particle products, composite formation, narrow particle-size distributions, low temperature post-calcinations, and they are cost effective, environmentally benign, and easily scalable [2]. Herein, a facile approach for the synthesis of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  microrods was designed using a solvothermal route in ethylene glycol. Due to the interesting properties of iron phosphate-based alluaudite phases from their vacancy rich crystal structure,  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  has attracted our attention and we report in the present work this phase obtained by solvothermal synthesis route to meet the morphology and size requirements for the fabrication of cathode materials with excellent electrochemical performance [1,21,22]. The solvothermal synthesis of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  was followed by heat treatment to obtain samples with high crystallinity and small particle size. This may

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facilitate the penetration of electrolyte and lithium ions in electrode material, and could provide much more active sites. This may enhance the electrochemical performances of active material and, therefore can provide fast transport channels and reduce diffusion paths of lithium ions [23,24].

The aim of this work is to synthesize  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  as new electrode material for lithium-ion batteries through wet chemical synthesis in ethylene glycol (EG). EG as a reaction medium, plays an important role in both reducing the particle size and product defects [25]. The high thermal stability of iron phosphate-based alluaudite compounds and the vacancies in  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  structure are the main reasons for this material to deliver excellent electrochemical performance (cycling stability and rate capability). Additionally, the strong inductive effect of the  $(\text{PO}_4)^{3-}$  polyanion group moderates the energetics of the transition metal redox couple to generate their relatively high operating potentials as positive electrode. Recently R. Essehli et al. showed that iron phosphate-based materials also possess low active voltage for negative electrode application and these characteristics qualify  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  as dual electrode materials [26,27]. All above described properties make this material an attracting candidate electrode with promising electrochemical properties.

## 2. Experimental

### 2.1. Chemicals

Ammonium dihydrogen phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\geq 99\%$ , Acros), manganese nitrate ( $\text{Mn}(\text{NO}_3)_2$ , 99.98%, Alfa Aesar), hydrated iron(III) nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , 96%, Riedel-de Haën), sodium nitrate ( $\text{NaNO}_3$ ,  $\geq 90.0\%$ , Sigma-Aldrich) and ethylene glycol as the solvent were used as received without further purification.

### 2.2. Material synthesis

Uniform  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  microrods were successfully obtained by a solvothermal method in ethylene glycol. In this synthesis,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and  $\text{Na}(\text{NO}_3)$  solutions in ethylene glycol were mixed in a molar ratio of 3:2:2:4. The solution of 6 mmol  $\text{NH}_4\text{H}_2\text{PO}_4$ , 4 mmol  $\text{Mn}(\text{NO}_3)_2$ , 4 mmol  $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and 8 mmol  $\text{NaNO}_3$  dissolved in 60 ml of ethylene glycol was mixed vigorously for about 20 min. The reaction mixture was then sealed into a 125 ml teflon-lined stainless steel autoclave, sealed and heated at  $180^\circ\text{C}$  for 6 h in oven. After cooling down to the room temperature, apple green precipitate was obtained and washed three times with ethanol and water respectively. The powder product was dried in oven under vacuum for two hours at  $80^\circ\text{C}$  and post calcined at  $700^\circ\text{C}$  for 48 h under air to remove remaining ethylene glycol and achieve a highly crystallized and pure phase of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ .

Fig. 1 shows the low temperature solvothermal synthesis approach of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ . We have used ethylene glycol (EG) to decrease the solubility of the precursors, increase the number of nucleation sites, and thereby achieve smaller particle dimensions [21].

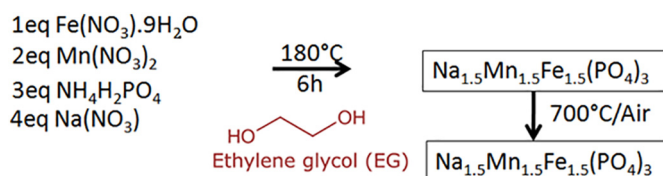


Fig. 1. Schematic representation of the solvothermal synthesis process of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$ .

### 2.3. Characterizations

The synthesized samples were characterized by powder X-ray diffraction (XRD) using a Bruker D8 diffractometer (Cu K $\alpha$  radiation).  $^{57}\text{Fe}$  transmission Mössbauer spectroscopy data were recorded by using a constant-acceleration spectrometer with a  $^{57}\text{Co}$  (Rh) source at room temperature. The Mössbauer spectral absorbers were prepared with 30 mg of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  materials mixed with boron nitride. The spectrometer was calibrated at room temperature with the magnetically split sextet spectrum of a high-purity  $\alpha\text{-Fe}$  foil as the reference absorber. The measurements were carried out in the velocity ranges a ( $\pm 4$  mm/s) with optimal energy resolution. The Mössbauer spectra were fitted using one or two Lorentzian doublets using Fullham program. In this way, spectral parameters such as quadrupole splitting ( $\Delta$ ), isomer shift ( $\delta$ ), linewidth ( $\Gamma$ ) and relative resonance areas of the different spectral components were determined. The validity of fits was judged on the basis of minimizing the number of parameters and  $\chi^2$  values.

The morphology and particle size of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  samples were investigated by scanning electron microscopy. The SEM analysis of the  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  samples was performed on a FEG-ESEM XL30 (FEI) with an accelerating voltage of 15 kV under high vacuum.  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  powder samples were deposited on carbon tapes. Sputtering deposition was done with gold target under argon atmosphere (Balzers, SCD004, Sputter coater).

Electrochemical measurements were performed using coin cells assembled in an argon-filled glovebox. For preparing working electrodes, a mixture of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  nanostructures, acetylene black, and polyvinylidene fluoride (PVDF) at a weight ratio of 60:20:20 was pasted on stainless steel grids. The average mass loading was around  $1.8\text{ mg}\cdot\text{cm}^{-2}$ . In a typical cell, pure lithium foil served as counter electrode, and microporous polypropylene, 25 mm monolayer films served as separator between electrodes. The electrolyte consisted of a solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt%). Galvanostatic cycling tests of the assembled cells were carried out on Neware (China) system in the voltage ranges of 1.5–4.5 V and 0.03–3.0 V (vs  $\text{Li}^+/\text{Li}$ ) for positive and negative electrode, respectively.

## 3. Results and discussions

### 3.1. Material structure analysis

X-ray powder diffraction was used to investigate the structural properties and to check the phase purity. The crystal structure of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  was characterized by X-ray diffraction and the corresponding XRD pattern is shown in Fig. 2. All the diffraction peaks can be well indexed according to an alluaudite structure and C2/c space group. No impurities such as  $\text{FePO}_4$  and others, which often appear in the iron phosphate based phases synthesized by traditional routes at high temperature, are detected; there is no observable evidence of secondary phases. The  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  sample obtained after calcination at  $700^\circ\text{C}$  (NMFP-700 $^\circ\text{C}$ ) shows sharp peaks indicating high crystallinity [28].

The Rietveld refinement of the XRD pattern of  $\text{Na}_{1.5}\square_{0.5}\text{Mn}_{1.5}\text{Fe}_{1.5}(\text{PO}_4)_3$  was realized, and the experimental details are given in Table 1. Atomic coordinates and temperature factors are given in Table 2; they are in good agreement with those previously reported by Hatert et al. [11,12]. Site occupancy factors indicate that vacancies occur on the A(2)' site (Table 2), in good agreement with the ideal formula of the compound. The A(1) site is filled by Na, the M(1) site is filled by Mn, while the M(2) site contains 0.75  $\text{Fe}^{3+}$  and 0.21 Mn. The structural formula of the compound, calculated from the refined site occupancies (Table 2), corresponds to  $(\text{Na}_{0.64}\square_{0.36})(\text{Na}_{0.99}\square_{0.01})(\text{Mn}_{0.93}\square_{0.07})(\text{Fe}_{1.50}^{3+}\text{Mn}_{0.42}\square_{0.08})(\text{PO}_4)_3$ .

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