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Hydrothermal self-assembly of sodium manganese iron phosphate particles: Growth mechanism and electrochemical performance in lithium-ion battery

Claude Karegeya[a,b], Abdelfattah Mahmoud[a,*], Bénédicte Vertruyen[a], Frédéric Hatert[c], Rudi Cloots[a], Frédéric Boschini[a]

[a] GREENMAT, CESAM, Institute of Chemistry B6, University of Liège, 4000 Liège, Belgium
[b] Faculty of Sciences, College of Education, University of Rwanda, 5039 Kigali, Rwanda
[c] Laboratory of mineralogy B18, University of Liège, 4000 Liège, Belgium

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ABSTRACT

$Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ (NMFP) dandelion sphere-like particles were successfully synthesized via a hydrothermal route without addition of any templates or surfactants (laboratory and pilot scales). The hydrothermal reactor (pilot scale) is equipped with stirrer for continuous agitation of reagents during the reaction. The obtained materials were characterized by X-ray diffraction, Mössbauer spectroscopy and Scanning electron microscopy. Results show that $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ samples obtained from the reaction performed at laboratory scale have hierarchical dandelion sphere-like morphology and the dandelions consist of micro-/nano-rods. On the other hand, we obtained the self-assembly nano-rods morphology for the particles prepared using hydrothermal reactor. On the basis of the experimental results, a growth mechanism of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ self-assembly and dandelion sphere-like particles was proposed. Temperature and time of hydrothermal reaction are found to be crucial parameters in controlling the growth of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ particles. In addition, investigation of the effect of continuous stirring during the hydrothermal reaction shows that the reaction time can be optimized to obtain $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ with small particles size. The influence of stirring on the NMFP morphology has been clearly evidenced. Indeed, the stirring leads to homogeneous particles. Cycling studies have shown that the synthesized $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ dandelions materials exhibit specific discharge capacities of about 62 and 57 mAh g^{-1} equivalent to about 1.2 and 1.05 lithium ions de-intercalated at C/15 and C/10 current density respectively.

1. Introduction

The synthesis of particles with 3D structures has attracted more attention due to their interesting properties and potential technical applications [1–6]. 3D compound architectures are built from one dimensional (e.g. nanowires, nanotubes and nanorods) or two dimensional (e.g. nanoplates) nano/micro-particles which are spontaneously organized in a particular way [7]. These materials have shown promising properties in various fields, especially in energy storage and conversion as electrode materials and in biomedical applications [8–11]. 3D materials have been mainly obtained by soft chemistry synthesis methods and among others solvothermal and hydrothermal methods have been extensively used [12,13]. Hydrothermal and solvothermal syntheses are more effective and convenient in achieving a variety of hierarchical architectures due to their various advantages such as fast reaction kinetics, short processing times, phase purity, high crystallinity, high yield, homogeneous particle products, composite formation and narrow particle-size distributions [14].

During the last decades, the design and the tailoring of the particles with controlled morphology architectures under mild and at low-cost conditions has been an intensive research field. Nevertheless, this issue still remains a great challenge for chemists and material scientists [1]. Here we discuss the synthesis of alluaudite-type sodium manganese iron phosphate ($Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$), which was obtained by hydrothermal synthesis route, and crystallized in 3D dandelion morphology structure via self-assembly. Alluaudite materials have recently attracted increasing attention as promising cathode materials for next-generation sodium and lithium-ion batteries (NIBs and LIBs) [13–15]. The importance given to iron phosphate-based alluaudite group is due to their stability at high temperature, the presence of vacancies that allow easy intercalation of Na/Li-ions in their crystal structures as well as their environmental friendliness and low cost [16]. They theoretically exhibit low capacities due to their high molecular weight, but the alluaudite structure vacancies owing to their complementarities and

* Corresponding author.
E-mail address: abdelfattah.mahmoud@ulg.ac.be (A. Mahmoud).

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synergetic effect in the insertion/extraction process enhances their capacities and shows good cycling performances as cathode materials for LIBs and NIBs [17–19].

$Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ has not been studied as electrode material elsewhere. In this work, it has been well established that a strong correlation exists between the electrochemical properties and the morphology, size, and structure of the inorganic materials. The dandelion nano-/micro architecture may facilitate the entering of electrolyte, sodium or lithium-ions and could provide much more active specific surface. These can lead to fast transport, reduce diffusion paths of Li ions and good cycling performance. 3D dandelion architecture of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ phase has attracted our attention thanks to the interesting properties doted to alluaudite materials and 3D architecture. The objective of this work is the investigation and optimization of the synthesis conditions used in hydrothermal synthesis of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ phase. Relationship between structural, morphological characteristic and electrochemical properties will be presented.

2. Experimental

2.1. Synthesis of Na $_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ with 3D dandelion architecture

2.1.1. Synthesis in Teflon-lined stainless steel autoclave

The hydrothermal typical synthesis of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ material consists on mixing precursors solutions and suspensions and treating the mixture at moderate temperature. In this process, 4 mmol sodium dihydrogen phosphate ($NaH_2PO_4{\cdot}H_2O \geq 99.0\%$, Aldrich) and 8 mmol sodium nitrate ($NaNO_3$, ≥ 99.0%, Aldrich) solutions were mixed with 2 mmol manganese carbonate ($MnCO_3$, ≥ 99.9%, Aldrich) and 2 mmol iron oxalate ($FeC_2O_4{\cdot}2H_2O$, 99.0%, Aldrich) suspensions in 60 mL of milli-Q water. The mixture was stirred for 0.5 h under argon at room temperature. Then, the mixture was sealed into a 125 mL Teflon-lined stainless steel autoclave and heated in oven at various temperatures (180–220 °C) and during different durations (2–6 h). The final products were collected by gravimetric filtration, washed with water and ethyl alcohol several times for each one respectively, and then dried in electric oven under vacuum at 80 °C for 2 h.

2.1.2. Synthesis in hydrothermal reactor equipped with a stirrer

In similar way as the above synthesis reaction in teflon-lined stainless steel autoclave, the mixture of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ precursors was transferred in a hydrothermal reactor (Parr 4580, 5.5 L, up to 200 bar, 500 °C), then heated at 220 °C for 6 h. During this synthesis, the reaction undergoes a continuous agitation and sampling has been done every 0.5 h on the stirred hydrothermal reaction. Collected samples were washed and dried in similar conditions as the samples obtained using teflon-lined stainless steel autoclave.

2.2. Characterization

Powder X-ray diffraction (XRD) data was collected on a Panalytical PW-3710 powder diffractometer using FeK_α radiation ($\lambda = 1.9373$ Å), operating from $2\theta = 10$ to 100°. The crystal structure was refined by the Rietveld method, starting from the observed powder diffraction pattern and using the DBWS-9807 software [20].

The morphology and particles size of the prepared samples were observed by scanning electron microscopy (XL 30FEG-ESEM, FEI).

^{57}Fe transmission Mössbauer spectroscopy data were recorded by using a constant-acceleration spectrometer with a ^{57}Co (Rh) source at room temperature. The spectrometer was calibrated at room temperature with the magnetically split sextet spectrum of a high-purity α-Fe foil as the reference absorber. The measurements were carried out in the velocity ranges of ± 4 mm s^{-1} with optimal energy resolution. The Mössbauer spectra were fitted with three Lorentzian doublets using Fullham program. In this way, spectral parameters such as quadrupole splitting (Δ), isomer shift (δ), linewidth (r) and relative resonance areas of the different spectral components were determined for the pure sample obtained in laboratory scale way (in Teflon cup without stirring). The validity of fits was judged on the basis of minimizing the number of parameters and χ values.

Electrochemical measurements were performed using coin cells assembled in an argon-filled glovebox. For preparing working electrodes, a mixture of $Na_{1.5}Mn_{1.5}Fe_{1.5}(PO_4)_3$ dandelion structure, carbon black and polyvinylidene fluoride (PVDF) at a weight ratio of 60:20:20 was pasted on a stainless steel grid. The separator was a 25 mm monolayer polypropylene membrane (Celgard). Lithium foil was used as counter and reference electrodes. The electrolyte consisted of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v). Galvanostatic cycling tests of the assembled cells were carried out on Neware Electrochemical Test System (China) in the voltage range of 4.5–2.0 V (vs. Li^+/Li).

3. Results and discussions

3.1. Preparation of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ material

To study and design the hydrothermal synthesis mechanism of 3D $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ dandelion particle formation, reactions with various synthesis conditions were performed. The preparation of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ crystallized in 3D dandelion morphology was achieved with an interesting architecture that can be applied as electrode material for LIBs and NIBs. The experimental flowchart process of hydrothermal synthesis evolution of this phase in teflon-lined stainless steel autoclave (laboratory scale) and hydrothermal reactor (pilot scale) is illustrated in Fig. 1. The $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ particles prepared through a laboratory scale synthesis will be so called later LS-NMFP while the particles obtained by a pilot scale synthesis will be denoted PS-NMFP.

3.2. Structure characterizations

The X-ray diffraction patterns of the two samples (LS-NMFP and PS-NMFP) do not show any difference. Fig. 2 displays the powder X-ray diffraction pattern of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ sample prepared by laboratory scale hydrothermal synthesis route at 220 °C for 6 h. All Bragg peaks can be attributed to the pure and well crystallized $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ alluaudite [PDF 04-012-077]. Experimental

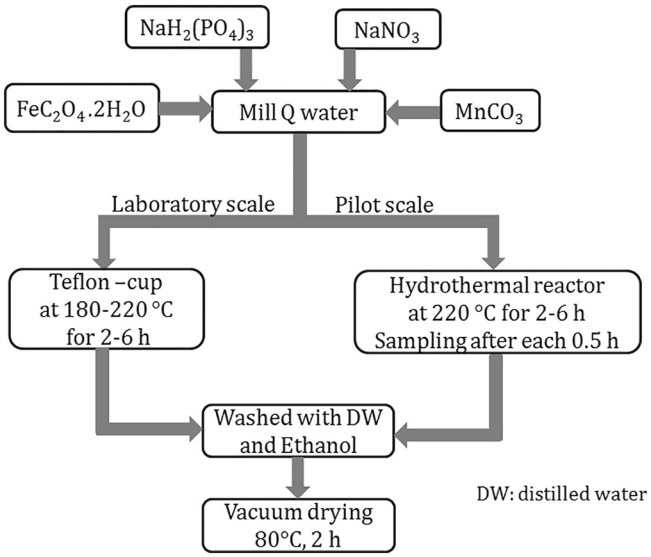

Fig. 1. The process flowchart for synthesis of $Na_2Mn_{1.5}Fe_{1.5}(PO_4)_3$ particles self-assembled in dandelion-like morphologies prepared via hydrothermal synthesis route in stainless steel autoclave and hydrothermal reactor.