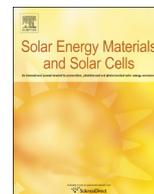




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Na₂FePO₄F/multi-walled carbon nanotubes for lithium-ion batteries: Operando Mössbauer study of spray-dried composites



Magali Brisbois^a, Sébastien Caes^a, Moulay T. Sougrati^b, Bénédicte Vertruyen^a, Audrey Schrijnemakers^a, Rudi Cloots^a, Nicolas Eshraghi^a, Raphaël P. Hermann^{c,d}, Abdelfattah Mahmoud^d, Frédéric Boschini^{a,e,*}

^a LCIS/GREENMAT, Institute of Chemistry B6, University of Liège, 4000 Liège, Belgium

^b Institut Charles Gerhardt, UMR 5253 CNRS, Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

^c Faculty of Sciences, University of Liège, 4000 Liège, Belgium

^d Jülich Center for Neutron Science JCNS and Peter Grünberg Institut PGI, JARA-FIT, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

^e APTIS, Institute of Physics, University of Liège, 4000 Liège, Belgium

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ABSTRACT

In order to favor electronic conductivity in sodium iron fluorophosphate electrodes for lithium- or sodium-ion batteries, composites of Na₂FePO₄F with multi-walled carbon nanotubes (CNTs) were prepared by pilot-scale spray drying. Addition of multi-walled CNTs in the solution results in an excellent dispersion of the CNTs within the volume of Na₂FePO₄F and not only at the surface of the particles. Following a heat treatment at 600 °C in argon in order to reach crystallization, X-ray diffraction and *ex situ* Mössbauer spectroscopy revealed the presence of significant amounts of Fe(III) and maghemite (γ-Fe₂O₃) in the powder. However, Na₂FePO₄F/CNTs composites exhibit good electrochemical performance when cycling against lithium, with a discharge capacity of 104 mA h g⁻¹ at C/10 rate and 90 mA h g⁻¹ at 1C rate. Therefore, *operando* ⁵⁷Fe transmission Mössbauer spectroscopy analyses were carried out in order to investigate the evolution of the iron oxidation state during cycling. During the first discharge, all the Fe(III) is reduced to Fe(II), explaining the good electrochemical performance.

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1. Introduction

The excellent performances of lithium iron phosphate [1] as positive electrodes in lithium-ion batteries have led to the widespread investigation of other low-cost, non-toxic iron phosphate-based compounds [2]. Sodium iron fluorophosphate Na₂FePO₄F is a promising candidate which was first reported by Ellis et al. [3]. Na₂FePO₄F is investigated both for lithium-ion batteries [3–10] and for sodium-ion batteries [8,11–13]. In lithium-ion batteries, at least one Na⁺ ion is progressively exchanged by Li⁺ during cycling: Na₂FePO₄F → NaFePO₄F + Na⁺ + e⁻ followed by NaFePO₄F + Li⁺ + e⁻ → (Li,Na)FePO₄F. The intercalation/deintercalation process takes place at a high voltage of 3.6 V vs. Li⁺/Li⁰ with a volume change of only 3.7% (compared to 6.7% for the LiFePO₄–FePO₄ couple). The Na₂FePO₄F structure [7,14–16] offers two-dimensional pathways for Li⁺ transport [4], but the electronic conductivity usually has to be improved through the preparation

of Na₂FePO₄F/C composite powders ensuring intimate contact between Na₂FePO₄F and conductive carbon. In most cases, a carbon source such as ascorbic acid [12], citric acid [6], sucrose [5,11], acetylene black [4], soot [10] etc. is included in the reactant mixture and the *in situ* formation of carbon is achieved by a heat treatment in inert atmosphere (typically argon), that also ensures the 2+ oxidation state of iron required in Na₂FePO₄F.

In a recent publication, we reported the pilot-scale synthesis of Na₂FePO₄F/C powders by the technique of spray-drying using citric acid as the carbon source [17]. Other reported synthesis methods for Na₂FePO₄F are solid-state reaction [3–5,9,10,12,18] and a few solution-based methods: hydrothermal [7], solvothermal in ionic liquid [8], sol-gel [3,6] and ultrasonic spray pyrolysis [11]. The advantages of the spray drying method are the good homogeneity of the precursors (as for other solution-based techniques) and the possibility to scale-up very easily from lab-scale to pilot-scale to production-scale.

As mentioned above, several carbon sources have been tested in combination with Na₂FePO₄F. However, composites of Na₂FePO₄F with carbon nanotubes (CNT) have not yet been reported. Extrapolating from numerous publications [19–24] on LiFePO₄/CNT, the high electronic conductivity (10³–10⁴ S cm⁻¹)

* Corresponding author at: LCIS/GREENMAT, Institute of Chemistry B6, University of Liège, 4000 Liège, Belgium. Tel.: +32 43663532; fax: +32 43663413.

E-mail address: frederic.boschini@ulg.ac.be (F. Boschini).

[24] of CNT is expected to enhance the electrochemical performance thanks to better conduction pathways for electrons. In order to take full advantage of the CNT properties, the synthesis process must lead to a homogeneous network of nanotubes.

In the present work, we report the synthesis of composite $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powders by pilot-scale spray-drying. The aqueous suspension to be spray-dried was obtained by dispersing CNT in the precursor solution. X-ray diffraction and *ex situ* Mössbauer spectroscopy were used to characterize phase purity after heat treatment at 600 °C in argon. The electrochemical performance of $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder vs. Li^+/Li^0 was then characterized at different cycling rates and *operando* ^{57}Fe transmission Mössbauer spectroscopy was used to investigate the evolution of iron oxidation state during cycling.

2. Material and methods

$\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ composite powders were prepared by a spray-drying process. In a typical experiment, a solution was prepared as described in [17] by adding iron powder to a solution of citric acid and glacial acetic acid in deionized water and further adding stoichiometric amounts of $\text{NH}_4\text{H}_2\text{PO}_4$, NaF and NaOH. Subsequently, multi-wall carbon nanotubes (AQUACYL X-A001, provided by Nanocyl sa) were dispersed into the solution under stirring, to reach a $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ weight ratio of 10/2. Deionized water was then added to reach a final iron concentration of 0.1 mol/l. The suspension was then spray-dried in a semi industrial spray-dryer (Niro Mobile Minor) with 25 ml/min feed rate at 140 °C inlet temperature. Finally, the spray-dried powders were heated at 600 °C for 12 h under argon flow.

The powders were characterized by X-ray diffraction (Cu $\text{K}\alpha$ parallel beam, D8, Bruker) and scanning electron microscopy (XL 30 FEG-ESEM, FEI). Mössbauer spectra were collected on a constant-acceleration spectrometer with a 50 mCi rhodium matrix cobalt-57 source calibrated at room temperature with an α -iron foil, which is issued as isomer shift reference. Electrochemical measurements were performed with Swagelok two-electrode coin cells assembled in an argon glove box. 13 mm diameter pellets were prepared by pressing, in a stainless steel grid, a mixture of $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder and polyvinylidene fluoride binder in 90:10 weight ratio. The counterelectrode was metallic lithium, the current collectors were stainless steel and the separator between electrodes was a 25 μm monolayer polypropylene membrane. The electrolyte used is 1 mol/l LiPF_6 in ethylene carbonate/dimethyl carbonate EC/DMC (1/1, v/v). Galvanostatic charge–discharge curves were measured using a PAR 263A potentiostat between 2.0 V and 4.5 V vs. Li^+/Li^0 at different cycling rates. *Operando* Mössbauer experiments were carried out using an electrochemical cell especially designed for this goal [25]. Using this electrochemical cell, 28 mg of active material (mixture of $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder and polyvinylidene fluoride binder in 90:10 weight ratio) was cycled vs. a Li negative electrode at a rate of C/50 in a 1 mol/l LiPF_6 EC–DMC electrolyte (1/1, v/v). Mössbauer spectra were collected during the insertion/deinsertion process every 5 h, with each spectrum being recorded for 5 h.

3. Results and discussion

Fig. 1 shows the diffractogram of the $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder after heating at 600 °C for 12 h in argon. The main diffraction peaks correspond to orthorhombic $\text{Na}_2\text{FePO}_4\text{F}$ phase. Additional reflections reveal the presence of two secondary phases: Na_3PO_4 and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). In an earlier publication [17] where no CNT were added, the same heat treatment resulted in a

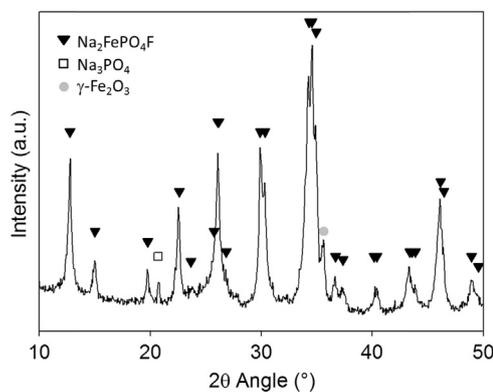


Fig. 1. XRD pattern of $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder after calcination at 600 °C for 12 h in argon.

diffractogram without secondary phases. There is no clear explanation for this apparent link between the presence of these secondary phases and the addition of CNT. Possibly, the presence of CNT might result in (i) inhomogeneities due to adsorption effects at the surface of CNT and/or (ii) modification of the iron oxidation behavior.

The dispersion of the CNT in the inorganic matrix was studied by scanning electron microscopy. Fig. 2a shows a SEM micrograph of the $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder after spray-drying. As usually observed for spray-drying of suspensions [26], the powder is made up of collapsed particles with typical diameters from a few microns to about 15 μm . This morphology is different from the spherical particles obtained in the absence of CNT (Fig. 2c) [17]. Fig. 2b and d shows that the morphology of the powders is retained after calcination. Higher magnification images in Fig. 3 show that the smooth surface (Fig. 3a) becomes granular due to crystallization (Fig. 3b) and that CNT are detected both at the surface of the particles (Fig. 3c) and within the walls of the collapsed spheres (see Fig. 3d showing a fractured particle). Some larger crystallites are seen in Fig. 3c and d; Energy Dispersive X-Ray analysis (EDX) does not reveal any significant difference in composition compared to other areas of the particles. Besides, these crystallites are similar in size to those observed at the surface of the particles in powders prepared without CNT [17]. Therefore, the crystallites seem to correspond to CNT-free crystallites, in agreement with the fact that they are observed at fractures in the walls of the collapsed particles or occasionally on the surface of these particles. Apart from these few crystallites, the microstructure study shows that spray drying of the suspension of multi-walled CNT in the precursor solution results in a good dispersion of the CNT within the $\text{Na}_2\text{FePO}_4\text{F}$ particles.

The $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder calcined at 600 °C in argon was also characterized by Mössbauer spectroscopy. Fig. 4 shows the experimental spectrum fitted with three doublets and one sextet; the spectral parameters and relative intensities are reported as an inset to Fig. 4. The sextet contribution represents about 13 at% (relative to total iron) and its isomer shift (δ), quadrupole splitting (ΔE_Q) and hyperfine field (H_{hf}) correspond to the maghemite phase ($\gamma\text{-Fe}_2\text{O}_3$) [27], already detected by X-ray diffraction. Amongst the three doublets, the main one (54 at%) has an isomer shift and a quadrupole splitting typical of Fe(II) in $\text{Na}_2\text{FePO}_4\text{F}$ [10], another much weaker (4 at%) doublet typical of Fe(II) is associated to structural defects [28], while the third doublet has an isomer shift $\delta=0.37$ mm/s and a quadrupole splitting $\Delta E_Q=0.71$ mm/s, typical of Fe(III) and amounting to 29 at%.

Despite this significant Fe(III) content, the electrochemical performance of the $\text{Na}_2\text{FePO}_4\text{F}/\text{CNT}$ powder calcined at 600 °C under argon atmosphere turns out to be rather good, as shown by galvanostatic charge–discharge cycles at different rates with a

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