



# Different electrochemical responses of $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ prepared by mechanochemical and solvothermal methods

Nina V. Kosova<sup>a,\*</sup>, Olga A. Podgornova<sup>a</sup>, Anton K. Gutakovskii<sup>b</sup>

<sup>a</sup> Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, 18 Kutateladze, 630128 Novosibirsk, Russia

<sup>b</sup> Rzhanov Institute of Semiconductor Physics SB RAS, 13. Pr. Acad. Lavrent'ev, 630090 Novosibirsk, Russia

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## ABSTRACT

A comparative investigation of the crystal structure, morphology and electrochemistry of  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  (LFMP) prepared by the mechanochemically assisted solid-state synthesis (SS) and the solvothermal synthesis (ST) was performed. The as-prepared samples were studied by XRD, FTIR, Raman, Mössbauer, SEM, TEM, galvanostatic cycling, GITT, and EIS. The low-temperature carbon-free LFMP-ST displays nanoplatelets with 20–30 nm thickness in the *b* direction and is characterized by the low concentration of the  $\text{M}_{\text{Li}}$  defects and more distorted  $\text{MO}_6$  octahedra compared to LFMP-SS. It shows poor conductivity and only one sloping voltage plateau at 3.4 V. Its post-coating with carbon at 750 °C leads to the appearance of two commonly observed plateaus, corresponding to the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox couples, and improves cyclability and rate capability. Carbon-coated LFMP-SS consists of irregular-shaped submicron particles and demonstrates two two-phase plateaus and an additional one at 3.6–3.7 V upon discharge. According to the GITT study, this plateau increases with cycling rate and is most likely controlled by the slower kinetics of the  $\text{Mn}^{3+}$  ions reduction.

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## 1. Introduction

$\text{LiMPO}_4$ -type materials with an ordered olivine structure have been extensively studied in the last decade as promising cathodes for lithium-ion batteries due to their excellent electrochemical properties and chemical and thermal stability [1]. The mixed-cation orthophosphates  $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4$  (hereinafter LFMP), which combine good rate capability of  $\text{LiFePO}_4$  and high potential of  $\text{LiMnPO}_4$ , are considered as the next generation of the olivine cathode materials because of low cost and environmentally benign. However, it was demonstrated [2] that the Mn-rich phase ( $y > 0.8$ ) in  $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4$  was not suitable for high specific capacity cathode material because of its intrinsic obstacles, that is, the strong electron ( $\text{Mn}^{3+}:3d^4$ ) lattice interaction (Jahn-Teller effect) in the charged state ( $\sim\text{Mn}_y^{3+}\text{Fe}_{1-y}^{3+}\text{PO}_4$ ) and the resultant limit to lattice distortion. Moreover, the solubility limit in the  $\text{Fe}^{3+}\text{PO}_4$ - $\text{Mn}^{3+}\text{PO}_4$  binary system lies in the composition range of  $0.6 < y < 0.8$ . In this respect, the compositions close to  $y = 0.5$  were found as the most promising compositions for the 4 V cathode material and were extensively studied in recent years. On the charge-discharge curves

of LFMP, two two-phase plateaus are usually observed which correspond to two redox couples:  $\text{Fe}^{2+}/\text{Fe}^{3+}$  at 3.5 V and  $\text{Mn}^{2+}/\text{Mn}^{3+}$  at 4.1 V. LFMP, as well as LFP, are characterized by low electronic conductivity and slow lithium ion diffusion. Efforts to enhance the electrochemical performance of LFMP were focused on improving the electron transport in the bulk (by addition of the supervalent cations) or at the surface of the material (by coating with a conductive carbon layer), or on shortening the diffusion distance for both lithium ions and electrons by fabricating nano-sized materials with different morphologies (such as nanoparticles, nanoplates, nanosheets, etc.).

When preparing lithium metal phosphates, different synthetic methods or even minor changes in the experimental conditions usually result in altered crystal structure or microstructure of the final materials even within the same composition. The question whether the as-prepared LFMP sample is a solid-solution or a two-phase structured material is still debatable. In 2001, Yamada et al. [2] suggested that LFMP is a stable solid solution because of a linear lattice expansion caused by a minor difference in the ionic radii of the high-spin  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions. On the contrary, a recent study by Huang et al. [3] has shown that the LFMP samples prepared by the solvothermal method contain individual LFP and LMP phases. The authors of Ref. [3] supposed that these two structures are

\* Corresponding author.

E-mail address: [kosova@solid.nsc.ru](mailto:kosova@solid.nsc.ru) (N.V. Kosova).

randomly stacked and are characterized by a pronounced structural distortion of the  $\text{MO}_6$  ( $M = \text{Fe}$  or  $\text{Mn}$ ) octahedra. Moreover, the distortion of the  $\text{MO}_6$  octahedra increases with increasing Mn concentration in LFMP. The phase separation phenomenon due to the formation of the Mn-rich and Fe-rich domains in the colloidal plate-shaped  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  nanocrystals during the typical carbon-coating process under  $\text{Ar}/\text{H}_2$  was also reported by Paoletta et al. [4].

Besides structural aspects, there is also no common opinion on the mechanism of Li (de)intercalation in LFMP. Using first-principles calculations, Malik et al. [5] proved the existence of two low-temperature miscibility gaps separated by a solid-solution phase centered at the Li composition  $y = x$  in the  $\text{Li}_x\text{Fe}_{1-y}\text{Mn}_y\text{PO}_4$  system. The occurrence of a solid-solution range was explained by decreasing the driving force for phase separation when the Fe sites are diluted by Mn. Thereafter, the structural changes in LFMP during charge-discharge have been widely studied by many groups. Nevertheless, the occurrence of single-phase or two-phase regions in LFMP during  $\text{Li}^+$  extraction/insertion is still a matter of debate. The authors of several recent studies have come to different conclusions starting from a two two-phase mechanism to observation of a narrow [2] or even broad [6–9] single-phase intermediate region. Earlier, it has been reported the feasibility to drive the well-established two-phase room-temperature insertion process into a single-phase one for the 40 nm carbon-free LFP particles [10]. Gibot et al. [10] believe that the reason for this is the presence of defects and cation vacancies in nanostructured LFP. Recently, Paoletta et al. [4] observed a unique redox behavior with only a single broad peak for the  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  platelet-shaped nanocrystals (~10 nm thick and ~70 nm wide) synthesized by the colloidal method. The authors of Ref. [4] supposed that this is due to the uniform distribution of the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions in the lattice in contrast to their random distribution in the submicron LFMP sample prepared via the hydrothermal route. After a typical carbon-coating process in a reducing atmosphere, these nanoplatelets undergo a rearrangement of their cations into Mn-rich and Fe-rich domains (via segregation) and the redox process evolves at two distinct potentials of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Mn}^{2+}/\text{Mn}^{3+}$ . The authors [4] concluded that the degree of mixing of the transition metals in the cation columns in  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  platelets is the most likely factor that strongly influences their redox behavior. According to the simulations of the surface energy and surface structure of LFP with hexagonal platelet morphology prepared by hydrothermal method [11], LFP should exhibit Li vacancies in the top layer of the (010) surface, as well as decreased coordination number of the surface Li and Fe ions.

In this article, we searched for a correlation between the crystal structure, morphology and electrochemistry of submicron carbon-coated  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  prepared by the mechanochemically assisted solid-state synthesis and nanoplate-like carbon-free  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  prepared by the solvothermal synthesis and after its carbon coating.

## 2. Experimental

### 2.1. Material synthesis

The  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$  (hereinafter **LFMP**) samples were prepared by two different methods: the mechanochemically assisted solid-state synthesis (**SS**) and the solvothermal synthesis (**ST**). The **SS** synthesis was realized using simultaneous carbothermal reduction of the  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  precursors described elsewhere [12,13]. The mechanochemical activation (**MA**) of the stoichiometric reagent mixtures of  $\text{Li}_2\text{CO}_3$ ,  $\text{Fe}_2\text{O}_3$  ( $\alpha$ -modification),  $\text{MnO}_2$ ,  $(\text{NH}_4)_2\text{HPO}_4$ , and carbon “P 277” (from the Institute of Problems of Hydrocarbons Processing SB RAS, Omsk, Russia) using both as a reducing agent (in

amount necessary to reduce  $\text{Fe}^{3+}$  and  $\text{Mn}^{4+}$  to  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ ) and a covering agent (additional 3 wt%) was performed using a high-energy AGO-2 planetary mill (900 rpm) in an Ar atmosphere for 5 min. The activated mixture was subsequently annealed at 750 °C for 1 h under Ar flow (hereinafter **LFMP-SS(3%C)/750**). The presence of carbon creates a reducing atmosphere, preventing the oxidation of ferrous ions to ferric ones.

For the **ST** synthesis, we used  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{LiOH}$  in a molar ratio  $(\text{Fe}+\text{Mn}):\text{P}:\text{Li} = 1:1:3$ , respectively, as the starting materials, and ascorbic acid as a reducing agent to prevent oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in the aqueous solution. The precursors were prepared by dissolving the stoichiometric amounts of the reactants in the solution of  $\text{H}_2\text{O}:\text{EG} = 1:1$ . Thus obtained solution was mixed at  $\text{pH} = 9.0$  to form a gel and put in a stainless-steel autoclave with a Teflon vessel (fill factor 0.85). The autoclave was heated to 200 °C, kept at this temperature for 3 h, and then cooled down to room temperature. The product was collected by filtration. The as-prepared light-brown powder (**LFMP-ST/200**) was washed several times with deionized water and ethanol and then air-dried at 90 °C. To increase the crystallinity of the final product and to create carbon coating on the surface of its particles, the **LFMP-ST/200** sample was ball-milled with 3 or 20 wt% of carbon “P 277” for 1 min in an Ar atmosphere and then annealed at 750 °C for 1 h under Ar flow. Thus synthesized  $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4/\text{C}$  composites will be further referred as **LFMP-ST(3%C)/750** and **LFMP-ST(20%C)/750**, respectively.

### 2.2. Material characterization

X-ray powder diffraction (XRD) was performed using a Bruker D8 Advance diffractometer,  $\text{Cu } K\alpha$  irradiation ( $\lambda = 1.54181 \text{ \AA}$ ). The XRD patterns were collected over the range of 10–70° with a step of  $0.02^\circ \text{ s}^{-1}$  and uptake time of 0.3–0.5 s. Structural refinement of the XRD data was carried out by the Rietveld method using the GSAS software package. Fourier transform infrared spectra (FTIR) were measured with a Bruker Tensor 27 FTIR spectrometer in the 400–4000  $\text{cm}^{-1}$  range using pellets with KBr. Raman spectra were measured with a Triplemate SPEX spectrometer with a 488 nm argon laser line. Mössbauer spectra were recorded using an NZ-640 spectroscope (Hungary) with a  $\text{Co}^{57}$   $\gamma$ -ray source at room temperature. Particle size and morphology were investigated by scanning electron microscopy (SEM) using a Hitachi TM-1000 scanning electron microscope and by transmission electron microscopy (TEM) using a JEM-4000EX transmission electron microscope operated at 4000 kV with a point-to-point resolution of 0.16 nm. Carbon content in the final products was determined by the elemental analysis using a CNHS EURO EA 3000 analyzer.

For the electrochemical testing, the composite cathodes were fabricated by mixing 75 wt% of the active material (excluding the carbon coating part) with 20 wt% of carbon (including the carbon coating part) and 5 wt% of the PVDF/NMP binder. The **LFMP-ST(20%C)/750** electrode was mixed only with the binder in the proportion 95:5. The mixed slurry was then pasted on the aluminum foil to obtain the working electrodes. The loading density of the prepared samples was 2–3  $\text{mg cm}^{-2}$ , and an electrode diameter of 10 mm was used throughout. The working electrodes were vacuum-dried at 90 °C before cell assembly. The Swagelok-type cells were assembled in an argon-filled glove box with Li as an anode, 1M  $\text{LiPF}_6$  (Sigma Aldrich, 99.99%) solution mixed with ethylene carbonate (EC) and dimethyl carbonate (DMC) (Alfa Aesar, 99%) 1:1 by weight as an electrolyte, and a glass fiber filter (Whatman, Grade GF/C) as a separator. Cycling was performed using a galvanostatic mode at C/10–2C charge/discharge rates within the voltage range of 2.0–4.5 V vs.  $\text{Li}/\text{Li}^+$  at room temperature. The GITT measurements

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