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Na₂FePO₄F as a Novel Cathode Material for Sodium and Lithium Accumulators*

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Abstract

A solid-phase waste-free and energy-saving synthesis with the use of mechanical activation of single-phase cathode material Na₂FePO₄F (sp. gr. *Pbcn*) for sodium and lithium accumulator has been implemented. It has been demonstrated that the product is formed already at the stage of mechanical activation (MA) and is crystallized in the course of subsequent annealing up to 600 °C, whereas heating up to 700 °C results in decomposing the product formed to give Na₃PO₄, Fe₃O₄, Na_{0.11}FeF₃ и Na₃Fe₂(PO₄)₃. Electrochemical properties of Na₂FePO₄F have been studied in a cell with a lithium anode and lithium electrolyte. According to results of the studies the specific capacity of Na₂FePO₄F surface-modified with carbon is equal to 115 mA · h/g at a rate of cycling amounting to C/10. It has been found that the process of chemical and electrochemical replacing Li by Na in the structure of Na₂FePO₄F is completed by the formation of a compound with the composition NaLiFePO₄F (sp. gr. *Pbcn*).

Key words: Na₂FePO₄F, mechanochemical synthesis, crystal structure, chemical and electrochemical exchange of Na for Li

INTRODUCTION

At the present time, it is difficult to imagine portables devices without lithium-ion rechargeable cells (LIC), but the world's reserves of lithium are limited. Replacing the LIC could be realized *via* using sodium-ion rechargeable cells, since sodium is widely distributed in the Earth's crust and oceans. Sodium-ion rechargeable cells, possessing a sufficiently high energy capacity are much cheaper as compared with LIC. The operation principle of sodium-ion rechargeable cells is similar to the principle of LIC operation: it is based on the reversible intercalation/deintercalation of alkali metal in the structure of the cathode and anode. However, carbon materials as an anode material in sodi-

um-ion rechargeable cells are not used, since sodium ions do not intercalate into the inter-layer space of graphite due to the larger ionic radius thereof as compared to the radius of the lithium ions. As anode material, one typically uses sodium metallophosphates (*e. g.*, NaTi₂(PO₄)₃), complex oxides of sodium and *d*-metals (Na₂Ti₃O₇, NaVO₂) and different sodium alloys (NaSi, NaGe), having a low potential [1]. As an electrolyte, solutions of sodium salts in organic solvents are used.

Promising cathode materials for sodium-ion rechargeable cells are presented by fluorophosphates Na₂MPO₄F (M = Fe, Mn, Co, Ni) [2]. Theoretically, they can extract two sodium ions with the participation of two electrons of *d*-metal per formula unit (*e. g.*, at elevated temperatures [3]), having a high theoretical specific capacity (>240 mA · h/g). Furthermore, the structure of Na₂MPO₄F is characterized by a small change in the unit cell volume in the

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course of the charge-discharge cycle, which affects positively the stability of the cathode under cycling (mechanical tensions). These materials have two-dimensional, 2D channels ($\text{Na}_2\text{FePO}_4\text{F}$, $\text{Na}_2\text{CoPO}_4\text{F}$), and three-dimensional, 3D channels ($\text{Na}_2\text{MnPO}_4\text{F}$), for the transport of alkali metal ions, which promotes the intercalation-deintercalation process at high rate values. The disadvantage of these materials consists in a low electronic conductivity and ionic diffusion thereof.

The electronic conductivity of $\text{Na}_2\text{MPO}_4\text{F}$ ($M = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$) could be improved in the case of obtaining thereof in a nanosized state, or *via* making a highly conductive carbon surface coating and/or *via* doping. Decreasing the particle size down to a nanoscale level leads to increasing the electrode/electrolyte contact surface and to decreasing the diffusion distances for the alkali metal ions in the solid phase as compared to the cathode material of micron dimensions. Owing to this, the processes of charging and discharging the rechargeable cell proceed with a high rate [4]. Coating of cathode material particles with carbon promotes increasing the electronic conductivity.

Currently, iron and sodium fluorophosphate $\text{Na}_2\text{FePO}_4\text{F}$ is one of the most promising sodium-containing cathode materials. It is characterized by a high operation voltage (3.5 V) and theoretical specific capacity (124 mA · h/g per one electron). The material is capable of cycling both in a cell with the sodium anode and sodium electrolyte, and in a cell with the lithium anode and lithium electrolyte. In the case of cycling in a cell with the lithium anode, the Na in the structure $\text{Na}_2\text{FePO}_4\text{F}$ is gradually replaced by Li. In order to obtain $\text{Na}_2\text{FePO}_4\text{F}$ in the nanosized state, researchers use different synthesis methods. A material having the particle size of 50–200 nm, a narrow particle size distribution and the specific capacity of about 100–120 mA · h/g could be prepared using sol-gel and ion-thermal methods [5, 6]. However, these methods require for a great cost, expensive reagents, being in addition environmentally unfriendly. A product with the particles in the form of highly porous spheres of 500 nm in size was obtained *via* ultrasonic pyrolyzing a mixture of NaNO_3 , NaF, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, H_3PO_4 and sucrose with subsequent annealing for 10 h in a flow of argon, but the specific

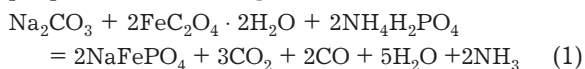
capacity thereof amounted up to only 90 mA · h/g [7]. With the use of mechanical activation (MA) of a mixture of, sodium carboxymethylcellulose in hot ethanol during 6 h and further annealing the precursor in a flow of argon and hydrogen during 10 h there were particles obtained with the size of 200 nm and the specific capacity equal to 118 mA · h/g [8].

Numerous studies demonstrated that a preliminary MA in energy-intensive activators results in grinding, homogeneous mixing, in the accumulation of energy in the form of defects in the mixture of initial reagents and in increasing the rate of diffusion in the solid phase. Owing to this the duration and temperature of the subsequent annealing decreases to a considerable extent and, as a result, materials in nanostructured state are obtained [9]. In some cases, it is possible to obtain the final product already at the mechanoactivation stage of MA. At the ISSCM of the SB RAS (Novosibirsk), this approach is under development in order to synthesize different electrode materials for LIC.

The purpose of this work is the preparation of $\text{Na}_2\text{FePO}_4\text{F}$ *via* a mechanically stimulated solid phase synthesis with further studying the structural and electrochemical characteristics thereof.

EXPERIMENTAL

The $\text{Na}_2\text{FePO}_4\text{F}$ cathode material was prepared in two stages:



The mechanical activation of the reaction mixtures was carried out in an AGO-2 planetary mill with the use of steel balls and drums. The subsequent annealing of the activated mixtures was performed in an argon gas flow at a temperature of about 600 °C. Additionally, we synthesized a sample of $\text{Na}_2\text{FePO}_4\text{F}$ with the carbon content of 3% in order to make a composite with electronically conducting carbon coating.

The structure of the samples obtained was investigated by means of X-ray powder diffraction (XRD) employing a Bruker D8 Advance diffractometer. The structure refinement was performed with the help of a Rietveld method using a GSAS software package [10].

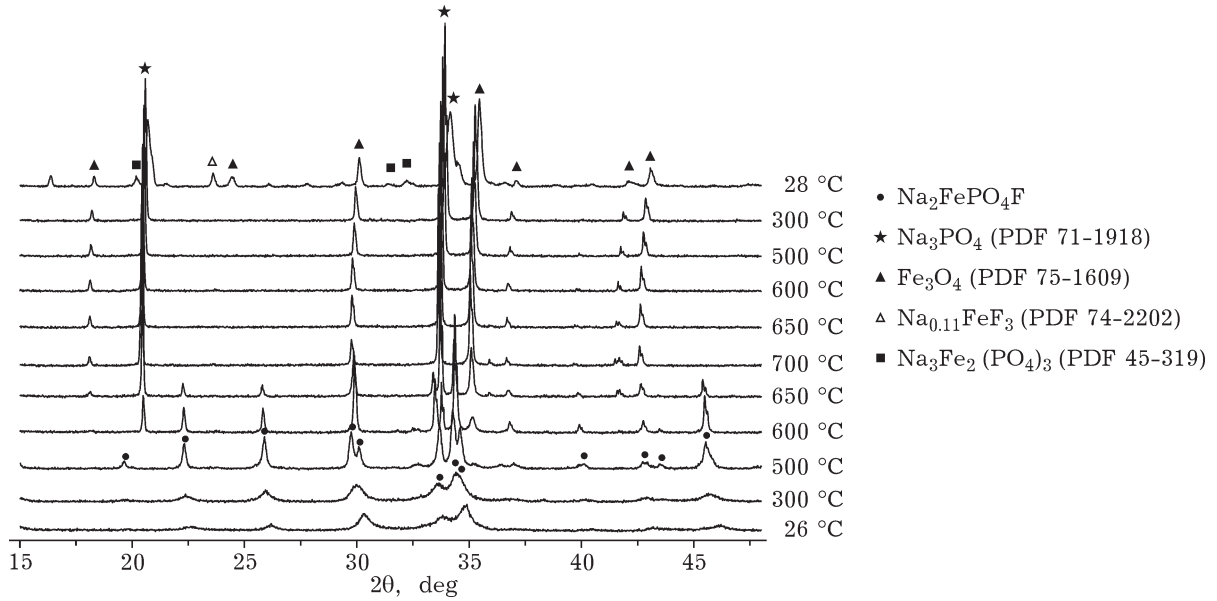


Fig. 1. *In situ* diffraction patterns of activated mixture of NaFePO₄ and NaF at heating and on cooling.

The *in situ* high temperature X-ray analysis was carried out on a Bruker D8 Advance diffractometer equipped with a HTK 1200N chamber of the in a flow of He within the temperature range from a room temperature to 700 °C at a heating rate equal to 0.2 °C/s and persistence time amounting to 300 s. The Mössbauer (NGR) spectra were registered using a NZ-640 NGR spectrometer (Hungary) at a room temperature (⁵⁷Co radiation source). The chemical shift was determined with respect to α-Fe.

The galvanostatic cycling was carried out in half-cell with a lithium anode and a 1 M LiPF₆ solution in a mixture of ethylene carbonate and dimethyl carbonate as the electrolyte at a room temperature, with the use of an automatic unit for cycling. The current strength was varied within the range of 0.1–10 mA. The chemical ion substitution of Na by Li in Na₂FePO₄F was carried out under stirring thereof in a 1 M LiBr solution in acetonitrile for 30 h according to a technique described by the authors of [5].

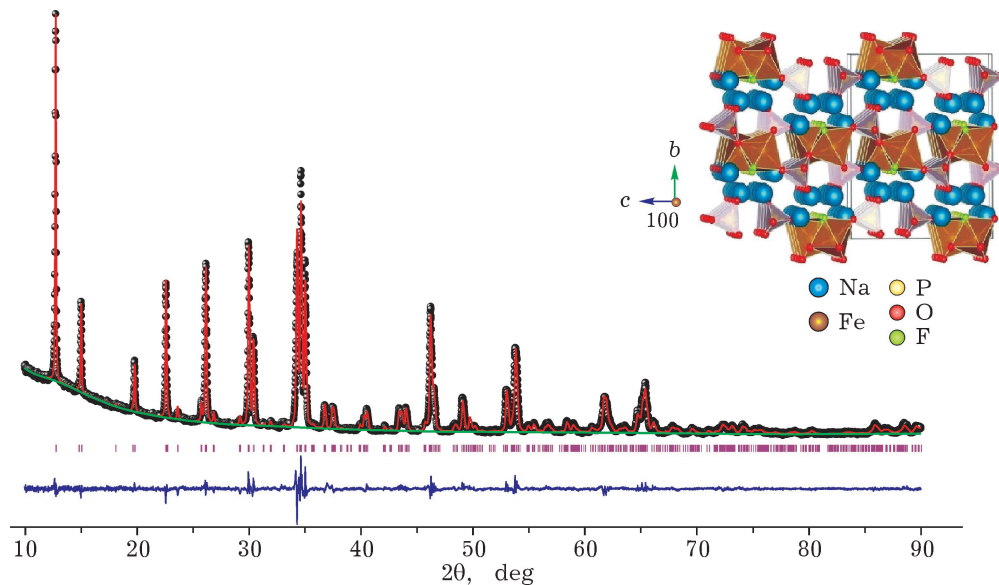


Fig. 2. Structure and diffractogram profile of Na₂FePO₄F refined according to Ritveld method.

TABLE 1

Refined structural parameters of $\text{Na}_2\text{FePO}_4\text{F}$ (sp. gr. *Pbcn*: $a = 5.2273(4)$ Å, $b = 13.821(1)$ Å, $c = 11.749(1)$ Å, $V = 848.8$ (2) Å³, $R_{\text{wp}} = 5.76$ %, $\chi^2 = 3.046$; filling 1.0)

Atoms	Position	x	y	z
Fe	8d	0.2368(5)	0.0099(2)	0.3253(1)
P	8d	0.2033(7)	0.3824(2)	0.0875(2)
Na (1)	8d	0.259(1)	0.2415(4)	0.3252(3)
Na (2)	8d	0.2524(9)	0.1285(9)	0.0853(2)
F (1)	4c	0	0.1242(6)	0.25
F (2)	4c	0	0.1005(5)	0.25
O (1)	8d	0.269(1)	0.3847(4)	0.0411(5)
O (2)	8d	0.288(1)	0.2803(5)	0.1351(4)
O (3)	8d	0.0979(9)	0.3967(5)	0.1057(4)
O (4)	8d	0.341(1)	0.4650(4)	0.1484(4)

RESULTS AND DISCUSSION

According to literature data, $\text{Na}_2\text{FePO}_4\text{F}$ crystallizes in the orthorhombic system, sp. gr. *Pbcn*. In the structure of $\text{Na}_2\text{FePO}_4\text{F}$, Fe atoms are located in octahedral positions 8d being surrounded by four oxygen atoms and two fluorine atoms. Two adjacent octahedra are connected with faces to form bioctahedron $[\text{Fe}_2\text{O}_6\text{F}_3]$, which bioctahedron, in turn, is connected with two adjacent bioctahedras *via* vertices. Na atoms are located in two different 8d positions, whereas the surrounding thereof consists of five oxygen atoms and two fluorine atoms. The phosphorus atom in 8d position is

located a tetrahedral environment of oxygen atoms typical for the former.

According to the results of XRD phase analysis, the final product, *viz.*, $\text{Na}_2\text{FePO}_4\text{F}$, is formed already at the stage of the mechanical activation of the initial NaFePO_4 and NaF mixture (Fig. 1), which indicates that a direct mechanochemical synthesis occurs. Heating the activated mixture in a high temperature chamber is accompanied by a gradual crystallization of the product, which finishes at the temperature of 600 °C. Further heating up to 650 °C and above causes decomposition of the resulting product, being completed at 700 °C. In this case, reflexes of $\text{Na}_2\text{FePO}_4\text{F}$ disappear on diffraction patterns. Decomposition products after a complete cooling the mixture are Na_3PO_4 , Fe_3O_4 , $\text{Na}_{0.11}\text{FeF}_3$ and $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$. Further for $\text{Na}_2\text{FePO}_4\text{F}$ synthesis was 600 °C was used.

The XRD pattern of the product synthesized is completely consistent with well-crystallized $\text{Na}_2\text{FePO}_4\text{F}$, sp. gr. *Pnma* (Fig. 2). The structure refinement was performed according to the Rietveld method, with describing the reflexes by pseudo-Voigt functions; the background was described using an eighteenth degree Chebyshev polynomial [10]. The structural filling and thermal parameters were not varied. The refined lattice parameters and atomic positions are presented in Table 1. The refining results obtained correlate with the literature data [5].

The NGR spectrum of the sample of $\text{Na}_2\text{FePO}_4\text{F}$ synthesized consists of a doublet, typical for Fe^{2+} ions in the octahedral environ-

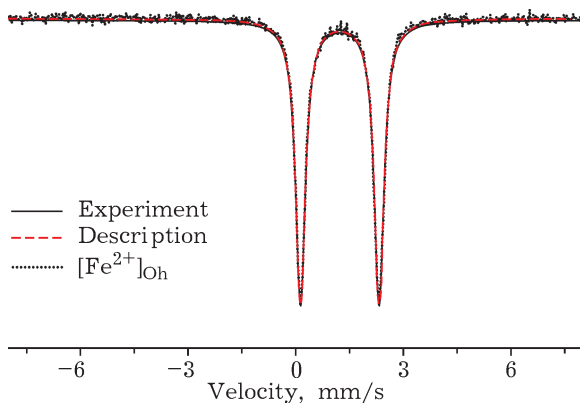


Fig. 3. NGR spectrum of $\text{Na}_2\text{FePO}_4\text{F}$.

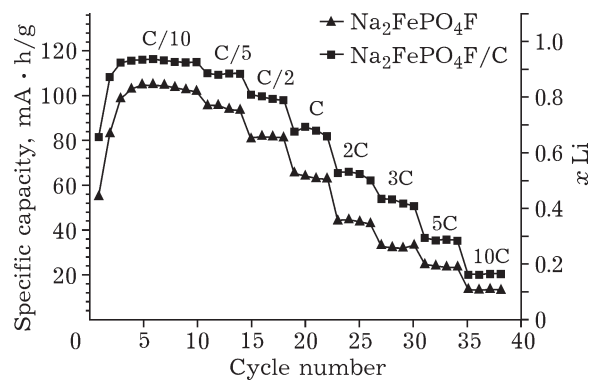


Fig. 4. Specific discharge capacity of $\text{Na}_2\text{FePO}_4\text{F}$ and $\text{Na}_2\text{FePO}_4\text{F}/\text{C}$ depending on the rate of cycling.

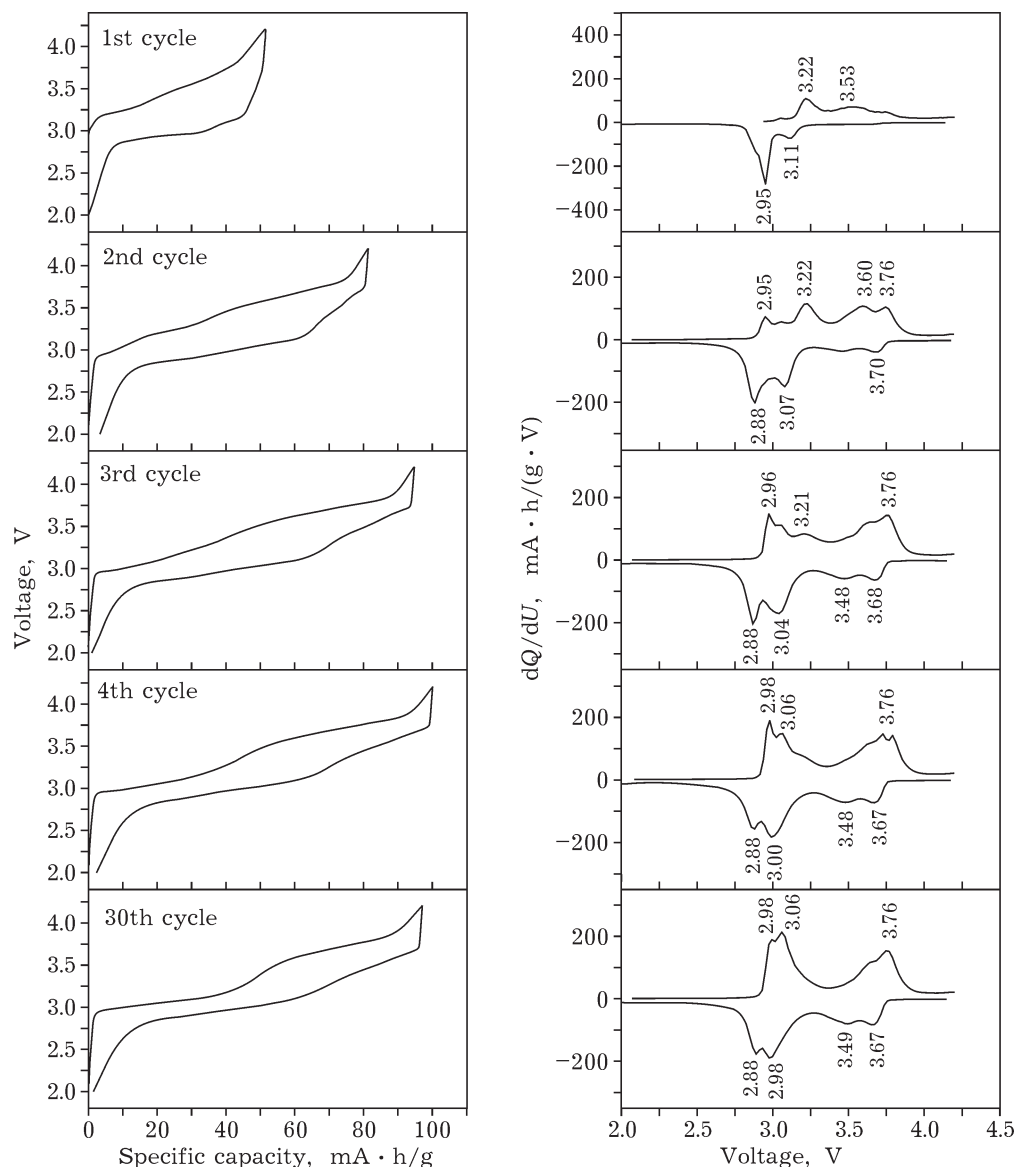


Fig. 5. Cycling profiles and dQ/dU depending on voltage for Na₂FePO₄F.

ment, which is consistent with the data reported by the authors of [8] (Fig. 3). The chemical shift and quadrupole splitting values amount to 1.23 and 2.19 mm/s, respectively. Thus, it follows from XRD and NGR data that the sample obtained is a single phase product, *viz.*, Na₂FePO₄F. It should be noted that the literature search indicates only one publication [11] that describes the preparation of a single phase Na₂FePO₄F, however, the method of synthesis in this case is rather complicated.

Samples of Na₂FePO₄F and Na₂FePO₄F/C prepared by us were successfully cycled in a

cell with lithium anode and lithium electrolyte within the voltage range of 2.0–4.2 V at a room temperature. It has been found that the specific discharge capacity of Na₂FePO₄F amount to 100 mA · h/g (theoretical capacity value being of 124 mA · h/g) at the cycling rate equal to $C/10$ ($C = 124$ mA/g) (Fig. 4). The addition of 3% carbon to the reaction mixture, leads to the formation of composite Na₂FePO₄F/C, whereas the specific capacity of the product increases up to 115 mA · h/g, corresponding to 92.5% of the theoretical value. In the course of cycling at higher rate values, there is no

significant decrease in the capacity of $\text{Na}_2\text{FePO}_4\text{F}$ and $\text{Na}_2\text{FePO}_4\text{F}/\text{C}$. Thus, two-fold increasing the rate of cycling leads to the decrease in the specific capacity up to $92 \text{ mA} \cdot \text{h/g}$ in case of the material without the carbon coating and up to $109 \text{ mA} \cdot \text{h/g}$ in case of composite $\text{Na}_2\text{FePO}_4\text{F}/\text{C}$. With a 10-fold increase in the rate, the specific capacity exhibits a less than two-fold decrease: down to $63 \text{ mA} \cdot \text{h/g}$ for $\text{Na}_2\text{FePO}_4\text{F}$ and down to $80 \text{ mA} \cdot \text{h/g}$ for the composite with carbon. Even a 100-fold increase in the rate does not cause the loss of the entire specific capacity: for $\text{Na}_2\text{FePO}_4\text{F}$ for this value amounts to $13 \text{ mA} \cdot \text{h/g}$, and for the composite the value is equal to $20 \text{ mA} \cdot \text{h/g}$, *i. e.* there is an only six-fold decrease observed.

It has been found that in the course of the first four cycles, the profile of charge-discharge curves exhibits changing to a considerable extent, and the first charging curve is unreproducible. It is reflected well in the dQ/dU parameter depending on voltage (Fig. 5). The conversion of cycling curves into such a type allows judging the staging and the average voltage of intercalation/deintercalation. From the data presented in Fig. 5 it follows that in the course of several subsequent cycles the shape of curves $dQ/dU = f(U)$ exhibits gradually changing [5]. After four to five cycles there were no significant changes observed. It is obvious that all the changes in the charge-discharge curves and $dQ/dU = f(U)$ curves in the case of initial cycles could be attributed to a gradual substitution of Na ions in the structure of $\text{Na}_2\text{FePO}_4\text{F}$ by Li ions, which substitution is accompanied by an increase in the specific capacity up to the fifth cycle. After the completion of the ion exchange procedure, the capacity exhibits no changing. We believe that the intercalation processes involve

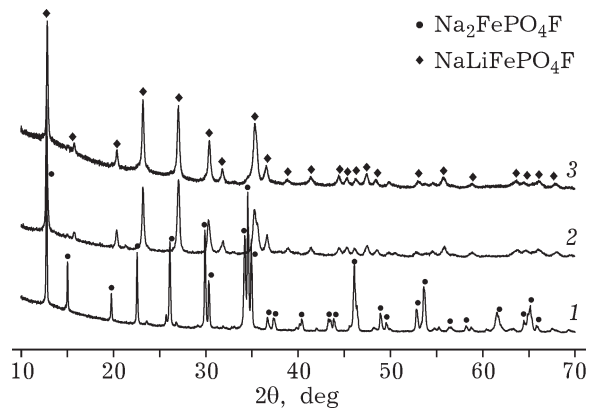


Fig. 6. Diffraction patterns of original $\text{Na}_2\text{FePO}_4\text{F}$ (1) and the products obtained resulting from the chemical (2) and electrochemical (3) ion exchange procedure.

predominantly Li^+ ions because of a considerable lithium excess in the cell.

Earlier the authors of [2] studied the chemical composition of the products resulting from the chemical oxidation-reduction of $\text{Na}_2\text{FePO}_4\text{F}$. First, the $\text{Na}_2\text{FePO}_4\text{F}$ was oxidized with NO_2BF_4 to obtain NaFePO_4F , and further the latter was reduced using a solution of 1 M LiI in acetonitrile. The resulting phase exhibited a composition of $\text{Na}_{0.75}\text{Li}_{1.25}\text{FePO}_4\text{F}$; the structure thereof differed from the $\text{Na}_2\text{FePO}_4\text{F}$ not only in the lattice parameters, but also in the redistribution of Na ions on between the two existing positions. It has been established that in the course of the electrochemical cycling of the $\text{Na}_2\text{FePO}_4\text{F}$ in the cell with lithium anode a phase with the composition of $\text{Na}_{0.6}\text{Li}_{1.4}\text{FePO}_4\text{F}$ forms; however, the structure of the product was not studied.

We investigated the crystal structure of products formed as a result of the chemical and electrochemical exchange substitution in compound $\text{Na}_2\text{FePO}_4\text{F}$ synthesized. The chemi-

TABLE 2

Lattice parameters for $\text{Na}_2\text{FePO}_4\text{F}$ and $\text{Na}_{2-x}\text{Li}_x\text{FePO}_4$ samples obtained *via* the chemical and electrochemical substitution (sp. gr. *Pbcn*)

Samples	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³
$\text{Na}_2\text{FePO}_4\text{F}$	5.2273(4)	13.821(1)	11.749(1)	848.8(2)
The same, after the chemical substitution	5.053(3)	13.804(6)	11.244(6)	784.0(1)
The same, after the cycling	5.028(2)	13.821(6)	11.199(5)	778.0(1)
$\text{Na}_{0.75}\text{Li}_{1.25}\text{FePO}_4\text{F}$ [2]	5.0407(3)	13.9069(9)	11.2215(5)	780.98(5)

cal ion substitution of Na with Li in the Na₂FePO₄F was carried out under its stirring in a 1 M LiBr solution in acetonitrile during 30 h. In case of performing the electrochemical exchange procedure the product was taken out of the cell after completing the discharge process. The diffraction patterns of the products are presented in Fig. 6. The structure refinement for the samples according to the Rietveld method demonstrated that, in both cases, the structure was similar to the one of original Na₂FePO₄F (sp. gr. *Pbcn*), however, the lattice parameters are substantially lower, since the ion radius of Li is smaller, as compared to Na ions. Parameters of the lattice calculated are presented in Table 2. Based on the parameters calculated, it has been established that the composition of the compounds could be described by the general formula NaLiFePO₄F.

CONCLUSION

It has been demonstrated that the single-phase cathode material Na₂FePO₄F can be obtained in the course of mechanochemically stimulated solid-phase synthesis, in this case the product is partly formed already at the MA stage, whereas the subsequent thermal annealing leads to its crystallization. The addition of carbon to the initial mixture leads to composite Na₂FePO₄F/C that exhibits improved electrochemical properties. The process of the chemi-

cal and electrochemical ion exchange of Na by Li in the structure of NaLiFePO₄F is completed by the formation of the product with the composition NaLiFePO₄F regardless of the method used, thereby; its structure in this case does not change (sp. gr. *Pbcn*).

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