

# Electrochemical properties of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ cathode materials produced by various synthesis methods and evaluation of the possibility of their use in sodium-ion batteries

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This article presents the results of a study of the electrochemical properties of cathodes based on polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by solid-phase synthesis and hot pressing. Factors affecting the electrochemical properties of cathodes based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by solid-phase synthesis, hot pressing, and sol-gel are established. The prospects of using  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  as a cathode material in sodium-ion batteries and the expediency of further modification of this compound in order to improve its electrochemical properties are substantiated.

**Keywords:** polycrystal; solid-phase synthesis; hot pressing method; cathode material; sodium-ion battery

## Introduction

Due to the demand and high cost of lithium-ion batteries, it is necessary to develop efficient sodium-ion batteries (SIB) [1], because sodium is more common

in nature, and its cost is much lower than that of lithium [2]. Nevertheless, so far, SIBs have a lower capacity and energy density than lithium-ion batteries (LIBs), and therefore are not competitive. Although, in the presence of effective SIB, they could be used both as current sources in portable electronics and in the power supply of electric vehicles, because these batteries are able to have a high specific energy capacity, resistance to multiple cycling, and a fast charge/discharge process [3, 4].

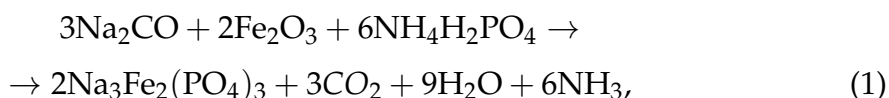
Polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can be referred to as a promising electrode material for SIA [5–8]. The  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  crystal structure belongs to the NASICON type structural class and consists of a three-dimensional anionic crystal framework  $\{[\text{Fe}_2(\text{PO}_4)_3]_{3-}\}_{3\infty}$  and sodium cations [9]. In [9], superstructural distortions were found in an  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  single crystal. When heated in  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , successive phase transformations occur from the monoclinic (with sp. gr. C2/m)  $\alpha$ -phase to the rhombohedral (3Rc)  $\beta$ -phase with superstructural reflections and then to the rhombohedral  $\gamma$ -phase, respectively [9, 10].  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is characterized by the presence of a superstructural unit cell with an antiferroelectric (ASE) type of dipole ordering, although ionic conductivity was found in it [10].

A porous cathode material based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by the sol-gel method is capable of generating an initial specific discharge capacity of up to 92.5 mAh  $\text{g}^{-1}$  in SIB [11]. In [11, 12],  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is considered as a promising anode material for aqueous SIB. Therefore, further investigation of the electrochemical properties of cathodes based on sodium-iron orthophosphate is highly relevant.

The purpose of this work is to study the electrochemical properties of 3 polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by solid-phase synthesis and hot pressing. In addition, it is important to establish the factors affecting the electrochemical properties of cathodes based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by solid-phase synthesis, hot pressing, and sol-gel, as well as to assess the prospects for their use as cathode materials for SIB.

## Experimental part

Polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  were obtained by two-stage solid-phase synthesis under normal conditions and under the action of hydrostatic pressure  $P=5 \cdot 10^5$  Pa. Samples were synthesized from the following reagents:  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{Fe}_2\text{O}_3$  (analytical grade). Solid-phase synthesis proceeded according to the following reaction:



The first group of samples was obtained by solid-phase synthesis at a temperature of 870 K for 8 hours (the first firing), and the second firing was carried out at a temperature of 970 K for 8 hours. The second group of samples differed from the first one in that the second stage of synthesis was carried out by hot pressing,

i.e. under the action of hydrostatic pressure  $P = 2 \cdot 10^5$  Pa and at a temperature of 970 K for 8 hours. The design and principle of operation of the installation for hot pressing were described in [9].

The main parts of a hot pressing plant include a pressing mechanism, a hanging furnace, alumina ceramic rods and a mold. A sample in the form of a tablet was placed in a mold containing a filling of zirconium oxide. Hydrostatic pressure on the sample was created using a pressing mechanism and alumina ceramic rods and backfill. The required temperature for firing the sample was created using a hinged furnace, and the temperature was controlled using a chromel-alumel thermocouple and a V7-21 voltmeter.

During the first firing of the charge, the  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  phase was formed. In both cases, during the second firing, the  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystalline structure was formed. However, the samples obtained by hot pressing had a higher density compared to the samples obtained at atmospheric pressure. It is possible that the effect of hydrostatic pressure on the sample is reduced to the creation of an internal stress in it and contributes to the partial removal of the monoclinically distorted crystal structure of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ .

The phase belonging and structural parameters of the synthesized polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  were studied by powder X-ray diffraction methods using a Bruker diffractometer ( $\text{CuK}\alpha$  radiation). Electrochemical measurements were carried out in a standard setup using a P-20X8 potentiostat. The composite cathode was composed of various materials with a mass ratio of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  80%, 10% carbon black (Alfa Aesar), and 10% polytetrafluoroethylene (Sigma-Aldrich). This mixture was milled with a planetary mill using ethanol for 2 hours. The average amount of electrode composite material was 10 mg. Cathode electrodes were fabricated in vacuum and dried in an oven at 120 °C for 12 hours. After flattening the manufactured mass under pressure, electrodes were obtained in the form of disks. The electrochemical cells were assembled in a sealed box filled with argon using pure sodium foil, which was considered as the anode. 1 mol of  $\text{NaClO}_4$  dissolved in ethylene carbonate and dimethyl carbonate in a 1:1 volume ratio was used as the electrolyte. Glass fiber (Whatman, GF/D) was used as a separator. The area of stainless steel electrodes was 1 cm<sup>2</sup>. Galvanostatic cycling was measured at various current densities and potential ranges using an automated cycling setup. All electrochemical measurements were carried out at room temperature.

## Results and discussions

### Results of synthesis and X-ray study of $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ polycrystals

Polycrystalline samples of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by solid-phase synthesis and under the action of hydrostatic pressure had a dark brown color. Both samples were well sintered pellets 10 mm in diameter and 1.5 mm thick. Using a diffractometer, the single-phase nature of the prepared samples was established.

In Figure 1 shows only the powder diffraction pattern of polycrystalline sample of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  powder (Figure 1 a), obtained by solid-phase synthesis at room temperature ( $T=293 \text{ K}$ ), because no differences were found in the diffraction pattern of the sample obtained under the action of hydrostatic pressure. Probably, a hydrostatic pressure of one atmosphere is not able to significantly affect the structural parameters of the polycrystal  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ .

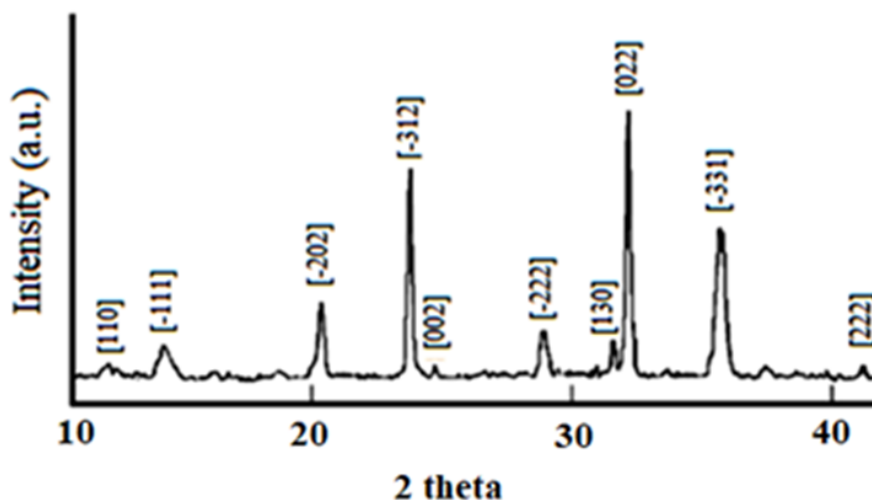


Figure 1. Powder X-ray diffraction pattern of polycrystal  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  (CuK  $\alpha$  -radiation).

The unit cell of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  at room temperature has a rhombic syn-gony with monoclinic distortion with sp. gr.  $C2/m$ , the established structural parameters are presented in Table 1.

Table 1.

Structural data for polycrystalline sample of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ .

Compound	T, K	sp. gr.	Unit cell parameters						
			a, Å	b, Å	c, Å	$\alpha^0$	$\beta^0$	$\gamma^0$	V/Z, Å <sup>3</sup>
$\alpha$ -phase									
$\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$	293	$C2/m$	15.125	8.726	21.571	90.2	-	237.1	240. 0

Given in Table 1, the unit cell parameters for the polycrystal  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  are comparable with the literature data of the authors presented in [9–11].

## Electrochemical properties of cathodes based on $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ polycrystals

The electrochemical characteristics of the synthesized samples were studied in sodium cells by galvanostatic cycling. Cycling of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  was carried out at a rate of 0.5 C in the voltage range of 1.5–3.5 V. Figure 2 shows the charge-discharge CV curves obtained in a cell with a sodium anode and a cathode based on a hot-pressed  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal (see curves 1 and 1'). The results were obtained in the voltage range of 1.5–3.5 V. Also in Figure 2 shows the CV characteristics of cathode materials based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by solid phase synthesis (curves 2 and 2'). For a comparative assessment of the

CV characteristics of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystals, Figure 2 (see curves 3 and 3') shows the characteristics of the sample obtained by the sol-gel method at SIB [11].

It can be seen from the presented results that the technological factor in the synthesis of samples has a significant effect on the electrochemical characteristics of the samples. First, the results of the charge-discharge CV-characteristics shown in Figure 2 (curves 1 and 1') indicate the existence of a small capacity of  $\approx 60$  mAh/g in SIB at a voltage of 2.5 V, but retain stable cycling when used in an electrochemical cell of a cathode based on a hot-pressed  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal. Nevertheless, the capacity of the cathode formed on the basis of the  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal obtained by hot pressing has a higher capacity compared to the cathode obtained by solid-phase synthesis (63 mAh/g).

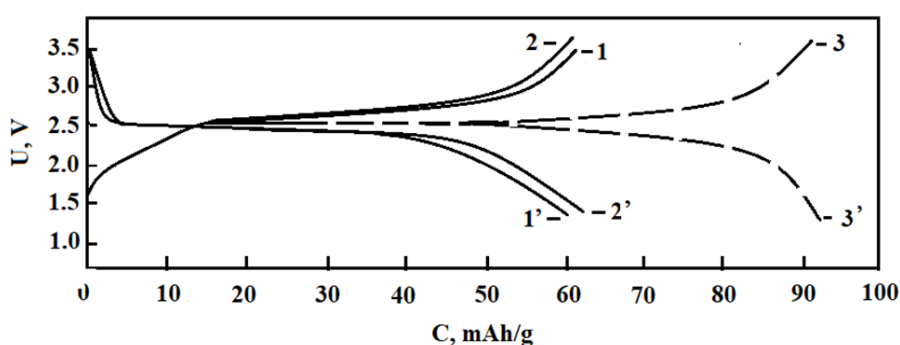


Figure 2. Charge-discharge curves (VC) that determine the specific discharge capacity (per 0.5 C) of cathode materials based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by the following methods: solid-phase synthesis (charge-discharge curves 1 and 1'), hot pressing (curves 2 and 2') and the sol-gel method (curves 3 and 3') in NIB (curves 3 and 3' correspond to the sample synthesized by the sol-gel method and obtained by the authors of [11]).

In all likelihood, the formation of the polycrystal  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  under the action of hydrostatic pressure contributes to the partial removal of the monoclinic distortion of the  $\{[\text{Fe}_2(\text{PO}_4)_3]_{3-}\}_{3\infty}$  crystal framework, which can slightly increase the conductive properties of the sample.

From the presented experimental data on the specific capacity of the samples (see curves 1, 1' ; 2, 2' ; 3 and 3' in Figure 2), one can theoretically calculate the number of charge carriers ( $n$ ), i.e. sodium ions ( $\text{Na}^+$ ) involved in the electrochemical processes of the discharge charge in the SIB according to the formula:

$$N = \frac{CM}{F}, \quad (2)$$

where  $C$  is the theoretical specific capacity of the battery electrode materials;  $F$  is Faraday's constant ( $96485 \text{ C/mol} = 26805 \text{ mAh/mol}$ );  $M$  is the molar mass, g/mol.

The calculation data for the number of charge carriers  $n$  of the samples under study are presented in Table 2.

Table 2.

Calculated data for the number of charge carriers ( $n_{Na}$ ) for polycrystalline samples of  $Na_3Fe_2(PO_4)_3$  synthesized by various methods.

Methods for the synthesis of polycrystalline samples $Na_3Fe_2(PO_4)_3$	Specific capacitance of electrode materials based on $Na_3Fe_2(PO_4)_3$ , C, mAh/g	Estimated number of charge carriers (sodium cations) $n_{Na}$
Samples obtained by solid phase synthesis under normal conditions	53	525
Samples obtained under the action of hydrostatic pressure $P=2 \times 10^5$ Pa	55	571
Samples obtained by the sol-gel method	67	779

A small number of charge carriers in  $Na_3Fe_2(PO_4)_3$  can be explained by the fact that for dipol ordered structures of the AFE type, the unit cell volume is typically doubling, therefore, out of 40 atoms of the unit cell double volume, only 6 are sodium cations. Since 4 sodium cations are needed to create an AFE-type dipol ordering, 2 of them can participate in conduction.

The calculation data show (see Table 2) that there is an insignificant increase in the specific capacity of the cathode based on  $Na_3Fe_2(PO_4)_3$  synthesized under the action of hydrostatic pressure than in the cathode made from a sample synthesized under normal conditions. Such an increase in the specific capacity of the cathode based on  $Na_3Fe_2(PO_4)_3$  (synthesized under the action of hydrostatic pressure) can be associated with a corresponding increase in the concentration of charge carriers ( $Na^+$ ) participating in the charge-discharge processes in the SIB (Table 2). Probably, the hydrostatic pressure promotes an increase in the symmetry of the monoclinically distorted  $Na_3Fe_2(PO_4)_3$  crystal, which can lead to an increase in the concentration of charge carriers ( $Na^+$ ) and the ionic conductivity of the sample.

Secondly, the  $Na_3Fe_2(PO_4)_3$  porous structure synthesized by the sol-gel method has a noticeably large residual capacity of  $\approx 67$  mAh  $g^{-1}$  in SIB. It is possible that the increase in the specific surface area is associated with the porosity of the  $Na_3Fe_2(PO_4)_3$  structure, which will contribute to the accumulation of sodium and improve the flow of electrochemical processes. Let us analyze the results of studying the electrochemical properties of  $\alpha - Na_3Fe_2(PO_4)_3$  obtained by various methods in terms of the prospects for using them as cathode materials for SIB.

It is known that the cathode material determines the main energy characteristics of SIB, namely, the operating voltage and electrochemical capacitance. Based on the data [1, 13], it is possible to establish the requirements that cathode materials in metal-ion batteries (MIA) should have:

- it is necessary to have metal cations of variable valence in the anionic struc-

ture, which can exhibit different degrees of oxidation ( $\text{Fe}^{3+} / \text{Fe}^{2+}$ ,  $\text{Mn}^{3+} / \text{Mn}^{2+}$ ,  $\text{V}^{4+} / \text{V}^{3+}$ , etc.);

- have the ability to intercalate and deintercalate mobile charge carriers;
- have the ability to generate high capacity at high operating potential;
- have high electrical conductivity;
- have small volumetric changes in the structure during the charge-discharge process.

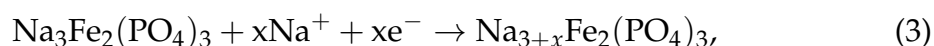
The results of the study of the electrochemical properties of  $\alpha\text{-Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by the methods: solid-phase synthesis (1), hot pressing (2) and the sol-gel method (3) allow us to conclude that these materials meet most of the above requirements, therefore, they have prospects for use as cathode materials in NIA.

### **Evaluation of the possibility of using polycrystals $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ as cathode materials for sodium-ion batteries**

The use of an  $\alpha\text{-Na}_3\text{Fe}_2(\text{PO}_4)_3$  type structure as a cathode material attracts attention due to the "openness" of the conduction channels between the A and B cavities in the unique 3D crystal structure and meets many requirements for cathode materials [11, 13].

The basis of the anionic crystal structure of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is the framework  $\{[\text{Fe}_2(\text{PO}_4)_3]_{3-}\}_{3\infty}$  (or "lantern block"). Such "lantern blocks" are coordinated with each other parallel to the [001] [11] direction. Iron and phosphorus are found in octahedral and tetrahedral polyhedra, respectively. Mobile sodium ions can be located in two crystallographic A- and B-cavities. The presence of extensive cavities and sufficiently free "conduction windows" between the A- and B-cavities of the crystal framework creates all the conditions for creating ionic conductivity. Electrode materials of the  $\alpha\text{-Na}_3\text{Fe}_2(\text{PO}_4)_3$  type are stable materials due to their open special 3D framework, good ionic conductivity and small volume changes during sodium intercalation/deintercalation processes. It also contains electrochemically active ions exhibiting different degrees of oxidation ( $\text{Fe}^{3+} / \text{Fe}^{2+}$ ), capable of creating high diffusion rates of sodium ions in the bulk of the material and high electrical conductivity (both in the bulk and along grain boundaries). The disadvantage of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is the very low electronic conductivity.

Since polycrystals  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by various methods are considered as cathode materials, it is necessary to consider the mechanism of ionic conductivity of these samples in the charge and discharge mode in an electrochemical cell. According to [4], the initial charge/discharge is specific and the capacity for  $\alpha\text{-Na}_3\text{Fe}_2(\text{PO}_4)_3$  is about  $61 \text{ mAh g}^{-1}$  with very flat plateaus at a voltage of about 2.5 V. The reversible capacity for  $\alpha\text{-Na}_3\text{Fe}_2(\text{PO}_4)_3$  was  $61 \text{ mAh g}^{-1}$  and maintained at  $57 \text{ mAh g}^{-1}$  after 500 cycles with no apparent loss of capacity. The ongoing charge processes can be described by a reaction of the form [5]:



Ionic conductivity in the samples under study can be described by the Arrhenius equation:

$$\sigma = \left(\frac{A}{T}\right) \exp\left(-\frac{E_a}{k_B T}\right), \quad (4)$$

where  $\sigma$  is the conductivity at temperature  $T$ ;  $k_B$  is the Boltzmann constant;  $E_a$  – activation energy;  $A$  is a pre-exponential factor that takes into account all of the above factors (except for the activation energy) that affect the ionic conductivity of the samples.

On the other hand, the Nernst-Einstein expression relates ionic conductivity to the diffusion coefficient of ions and is useful from the point of view of molecular dynamics, i.e. It is assumed that the conductivity is equal to:

$$\sigma = \frac{nq^2 D}{k_B T}, \quad (5)$$

where  $n$  is the number of mobile ions per unit volume;  $q$  is the charge of mobile ions;  $D$  is the self-diffusion coefficient of ions, which can be represented as follows:

$$D = \frac{zNc(1-c)a^2\nu}{k_B T}, \quad (6)$$

where  $z$  is the number of nearest neighboring cavities;  $N$  is the density of mobile ions;  $c$  is the concentration of ions;  $a$  is the distance between the cavities;  $\nu$  – the frequency of jumps of mobile ions is equal to:

$$\nu = \nu_0 \exp\left(-\frac{E_a}{k_B T}\right), \quad (7)$$

where  $E_a$  is the activation energy required for the ion to jump over the potential barrier and move into the neighboring cavity, and  $\nu_0$  is the frequency of ion jumps at  $T=0$ .

Expression (6) assumes that a high diffusion coefficient in solids requires a high density of mobile ions ( $N$ ) as well as the presence of free sites (which can be accessed by mobile ions) (see  $(1-c)$  in equation (6)).  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  has three-dimensional conduction channels in the  $\{[\text{Fe}_2(\text{PO}_4)_3]_{3-}\}_{3\infty}$  crystal framework, in which the number of vacant cavities is greater than the concentration of mobile sodium cations. The presence of a wide "conduction window" between the A- and B-cavities in the conduction channel forms low barriers between the cavities, which will allow free movement of conduction ions with low activation energy ( $E_a$ ).

Thus, the values of the diffusion coefficients of mobile ions and their activation energies are important parameters for the processes of intercalation and deintercalation. The parameters of cathode materials for  $\alpha$ - $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  are presented in Table 3.



Table 3.

Parameters of cathode materials based on polycrystalline samples of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ .

Parameters	$\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$	References
Specific discharge capacity, $C$ , $\text{mAh g}^{-1}$	55 at $U=2.5$ V (solid phase synthesis)	Experimental data
	57 at $U=2.5$ V (hydrostatic pressure synthesis)	
	61 $\rightarrow$ 57 at $U=2.5$ V (500 cycles)	[4]
	92.5 $\rightarrow$ 71.5 at $U=2.5$ V (500 cycles) for porous electrode	[11]
Theoretical specific discharge capacity, $C$ , $\text{mAh g}^{-1}$	120 at $U=2.5$	[11]
Diffusion coefficients in electrodes $D$ , $\text{cm}^2/\text{s}$	$4.67 \times 10^{-12}$	[14]
	$2.4 \times 10^{-8}$	[15]
	$1.65 \times 10^{-11}$ for porous electrode	[10]
Activation energy of sodium cation migration $E$ , eV	0.45	[6]

The parameters of cathode materials based on polycrystalline samples of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  presented in the Table 3 demonstrate acceptable electrochemical properties when used as cathode materials. For  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , the diffusion coefficient of  $\text{Na}^+$  ions is low and is about  $4.67 \times 10^{-12} \text{ cm}^2/\text{s}$ . However, depending on the production technology, polycrystalline samples of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  can have higher diffusion coefficients of  $1.65 \times 10^{-11} - 2.4 \times 10^{-8} \text{ cm}^2/\text{s}$ . In addition, the structure of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  is isotropic and the activation energy is low, 0.45 eV. Despite the low diffusion coefficient of  $\text{Na}^+$  ions, cathodes based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  not only provide acceptable electrochemical characteristics, but also attract attention due to the presence of stable and non-toxic Na and Fe elements. The performance of cathodes based on  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  in aqueous electrolytes is more attractive than in non-aqueous ones. Methods for improving the energy characteristics of SIB using  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  are already known. Thus, to increase the energy intensity of SIB, carbon-based coatings are applied to the electrodes [16, 17], i.e., the electronic conductivity of these materials is increased. Electrodes from  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  synthesized under the influence of hydrostatic pressure bring small but noticeable improvements in the power consumption of SIB. Despite the shortcomings of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  cathodes and low specific energy consumption in SIB, materials with a NASICON type structure are recognized as promising electrode materials for SIB, because By modifying the composition and structure, the electrochemical properties of these materials can be significantly improved.

## Conclusion

Based on the presented experimental results and analysis of the electrochemical activity polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by various methods, the following conclusions can be drawn:

1) The specific energy capacity of the cathode in the SIB composition, formed on the basis of the polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , obtained by hot pressing, has a higher energy capacity compared to the cathode made from the sample obtained by solid-phase synthesis. This result can be associated with an increase in charge carriers ( $\text{Na}^+$ ) (see Table 2) and ionic conductivity, due to the partial removal of the monoclinic distortion of the anionic crystal framework of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  under the action of hydrostatic pressure. (probably, at the moment of formation of the polycrystalline samples of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , partial symmetrization of the monoclinic distortion of the  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  anionic crystal framework occurs under the action of the applied hydrostatic pressure).

2) The specific energy capacity of the cathode in the composition of the SIB formed on the basis of the polycrystalline samples of  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by the sol-gel method is noticeably higher than with other indicated synthesis methods. Probably, the reason for this may be an increase in the specific surface of the polycrystal, associated with the porosity of the  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  structure, which will facilitate the accumulation of sodium and improve the course of electrochemical processes.

3) Polycrystalline samples of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  obtained by hot pressing and sol-gel can be good cathode materials for SIB, despite the low energy consumption, because these materials meet most of the requirements for cathode materials in SIB. In particular, they have structural stability during the charge-discharge process, and due to the polyanionic nature of the crystalline framework of these compounds, they are capable of fast charging/discharging and accumulating acceptable energy capacities in SIB.

4) From the point of view of the prospects for the use of this material in commercial SIB, there are still such shortcomings: as a low working potential of 2.5–3 V rel.  $\text{Na}^+ / \text{Na}$ , low electronic conductivity, which is the reason for the low energy density of the battery. Therefore, work is needed to further improve the electrochemical properties of cathodes based on the polycrystalline samples of  $\alpha - \text{Na}_3\text{Fe}_2(\text{PO}_4)_3$  polycrystal.

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