



Article

$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ Cathode Materials for Li-Ion Batteries: Synthesis and Characterization

Tatiana Gavrilova ^{1,*}, Yulia Deeva ², Tatiana Chupakhina ², Ivan Yatsyk ¹, Nikolay Lyadov ¹,
Ranis Garipov ¹, Nail Suleimanov ¹, Mikhail Khrizanforov ^{3,4} and Sergey Khantimerov ¹

¹ Kazan E. K. Zavoisky Physical-Technical Institute, FRC Kazan Scientific Center of RAS, Sibirsky Tract, 10/7, 420029 Kazan, Russia

² Institute of Solid State Chemistry UB RAS, Pervomaiskaya Str., 91, 620990 Ekaterinburg, Russia

³ Aleksander Butlerov Institute of Chemistry, Kazan Federal University, 1/29 Lobachevskogo Str., 420008 Kazan, Russia

⁴ Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Arbuzov Str., 8, 420088 Kazan, Russia

* Correspondence: tatyana.gavrilova@gmail.com

Abstract: $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ (LVPO/LPO) composites as cathodes for Li-ion batteries were synthesized by the hydrothermal method and subsequently annealed in an Ar atmosphere. The effect of Li_3PO_4 content on the crystal structure, morphology and the related magnetic and electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites, containing 7.5 wt% and 14 wt% of Li_3PO_4 (LVPO/LPO-7.5 and LVPO/LPO-14) was investigated. The microstructure and morphology of the obtained composites were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM); magnetic and electrochemical properties investigations were performed using the electron spin resonance and galvanostatic methods, respectively. It was shown that $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites exhibit a high discharge capacity, good cycle performance (105 and 120 mAh g^{−1} for the 200th cycle at 1C for LVPO/LPO-7.5 and LVPO/LPO-14, respectively), and insignificant changes in the surface morphology after 200 lithiation/delithiation cycles. Our results demonstrate that the increase in Li_3PO_4 content led to a decrease in the Li stoichiometry and magnetic inhomogeneity in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ phase; thus, the improvement in the electrochemical performance of LVPO/LPO composites due to incorporation of Li_3PO_4 can be attributed to their chemical and magnetic inhomogeneity.

Keywords: $\text{Li}_3\text{V}_2(\text{PO}_4)_3$; cathode material; electron spin resonance; discharge capacity



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1. Introduction

Nowadays, much research in the field of modernization of Li-ion batteries (LIB) is devoted to the development of high-energy-density materials for the so-called “post-lithium-ion batteries” [1,2]. Among others, oxides [3] and phosphorus-containing materials, as potential electrode materials for LIB, are of particular interest, e.g., orthophosphate vanadates as the cathode materials [4,5] and black phosphorus as the anode material [6]. Often, the orthophosphate vanadate $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVPO) is used as a cathode material in the form of a composite: pure LVPO or in the form of the partially substituted composition with carbon [7–14]. It is assumed that carbon can improve the electrochemical properties; at the same time, it is not a trivial task to obtain pure LVPO without carbon. On the other hand, it would be interesting to study a pure LVPO sample with a deficiency of lithium, assuming that its initial structure will be more predisposed to the Li intercalation/deintercalation process and more resistant to mechanical stress, therefore degrading less than was expected in the case of the nanostructured cathode materials with high energy density, high rate capability, and excellent cycling stability; this would be due to their huge surface area, short distance for mass and charge transport, and freedom for volume change [15]. However, lithium-deficient LVPO samples have not been studied in such detail to date [16,17], also

because of the major difficulty in controlling the oxidation degrees of vanadium, namely V(III), V(IV) and V(V), during the different synthesis processes [18].

At present, we have developed a method for composite synthesis without any carbon but containing Li_3PO_4 as an additional phase that makes this system promising in terms of improving the electrochemical properties [19,20]. Moreover, it was found here that the phase with a deficiency of lithium $\text{Li}_{3-x}\text{V}_2(\text{PO}_4)_3$ is stable formed in the composition of LVPO/LPO solid solutions.

It is known that to provide a high discharge capacity in a solid-state battery, which includes a Li- and V-containing polyphosphate compound and contains $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ as a main phase, the content of Li_3PO_4 should be up to 15.0 wt% with respect to $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [21]. In this regard, two type of samples were synthesized for further investigations of their structural, magnetic and electrochemical properties: (i) $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites containing 14 wt% of Li_3PO_4 (of which their composition is close to the above-mentioned limit) and (ii) $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites containing 7.5 wt% of Li_3PO_4 (one-half of the limit of Li_3PO_4 concentration).

2. Experimental Results

2.1. Sample Synthesis and Characterization

In this paper, the investigated $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites containing 7.5 wt% and 14 wt% of Li_3PO_4 (LVPO/LPO-7.5 and LVPO/LPO-14) that were obtained by the hydrothermal method with the subsequent annealing in Ar atmosphere. The synthesis was carried out according to the following scheme:

(i) Chemically pure vanadium (IV) formate $\text{VO}(\text{HCOO})_2 \cdot \text{H}_2\text{O}$, lithium carbonate Li_2CO_3 , and ammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ were used in stoichiometric molar ratios as starting materials, except for vanadium(IV) formate, which was used in a stoichiometric deficiency. The above-mentioned reagents were mixed to the homogenization stage in the hydrothermal synthesis autoclave reactor (100 mL) using 5 mL of distilled water.

(ii) The autoclaving was carried out at 200 °C for 10 h with the subsequent cooling at room temperature without air access. The resulting dark violet gel-like precursor was dried in a Petri dish at 100 °C.

(iii) The dried precursor was pressed and subjected to the carbothermal reduction: calcination at 800 °C in an argon flow during 5 h in the presence of carbon (5 wt%) in a separate crucible. Carbothermal reduction was used to exclude the oxidation of V^{3+} ions to the most stable oxidation states V^{4+} and V^{5+} . Moreover, the use of carbon makes it possible to prevent the possible formation of an impurity phase—the ammonium hexavanadate $(\text{NH}_4)_2\text{V}_6\text{O}_{16}$ —since the formation of the gaseous CO and CO_2 products is observed, which comprise a reducing medium.

It should be noted that the use of the hydrothermal synthesis method instead of thermal hydrolysis [22] made it possible to exclude the drying of the precursor in an argon flow. Due to higher pressure inside the hydrothermal synthesis autoclave reactor, the exposure time is almost 3.5 times less than the hydrothermal method. Moreover, the increased pressure due to the released carboxyl and nitrate volatile components promotes the process of the complete reduction of vanadium from V^{5+} to V^{3+} , which makes it possible to lower the phase formation temperature.

The composition of the obtained LVPO/LPO-7.5 and LVPO/LPO-14 samples was controlled using a Shimadzu XRD-7000 S automatic diffractometer with 0.03° steps in the 10° – 70° range with an exposure of 2 s at a point. The phase analysis of the reaction products was performed using the crystallographic database “Database of Powder Standard–PDF2” (ICDD, USA, Release 2005). X-ray pattern processing was performed according to the Rietveld method using the FULLPROF-2018 software. According to X-ray diffraction data, the resulting products were $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (92.5 wt%)/ Li_3PO_4 (7.5 wt%) and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (86 wt%)/ Li_3PO_4 (14 wt%) composites. The X-ray diffraction pattern of LVPO/LPO-14 sample is presented in Figure 1. The crystal structure parameters of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ and Li_3PO_4 phases are given in Table 1.

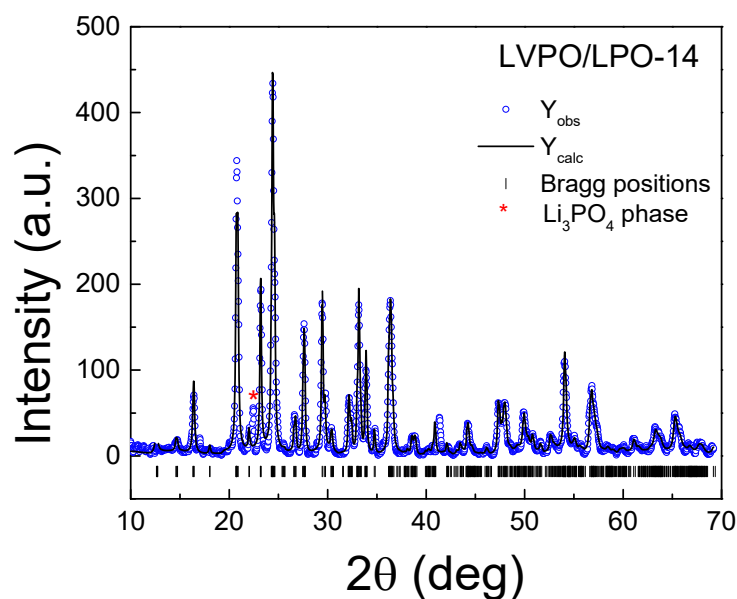


Figure 1. Experimental, theoretical, and differential X-ray diffraction pattern of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (86 wt%)/ Li_3PO_4 (14 wt%) composite.

Table 1. Crystal structure parameters of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites.

Sample	LVPO/LPO-7.5	LVPO/LPO-14
main phase	$\text{Li}_3\text{V}_2(\text{PO}_4)_3$, 92.5 wt%	$\text{Li}_3\text{V}_2(\text{PO}_4)_3$, 86 wt%
syngony	monoclinic	monoclinic
space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a , Å	8.606(1)	8.614(2)
b , Å	8.587(4)	8.595(3)
c , Å	12.032(1)	12.040(3)
β , °	90.554(1)	90.55(1)
V , Å ³	889.1(2)	881.6(2)
additional phase	Li_3PO_4, 7.5 wt%	Li_3PO_4, 14 wt%
syngony	orthorhombic	orthorhombic
space group	$Pnma$ (#62)	$Pnma$ (#62)
a , Å	6.146	6.146
b , Å	10.453	10.453
c , Å	4.913	4.913
V , Å ³	315.64	315.64

The morphology of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites was investigated using scanning electron microscopy (SEM) via an EVO 50 XVP scanning electron microscope. SEM images of the as-prepared LVPO/LPO-7.5 and LVPO/LPO-14 surfaces are shown in Figure 2a,b, respectively. In addition to the as-prepared samples, the morphology of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites was investigated during the lithium intercalation/deintercalation process (Figures 3 and 4).

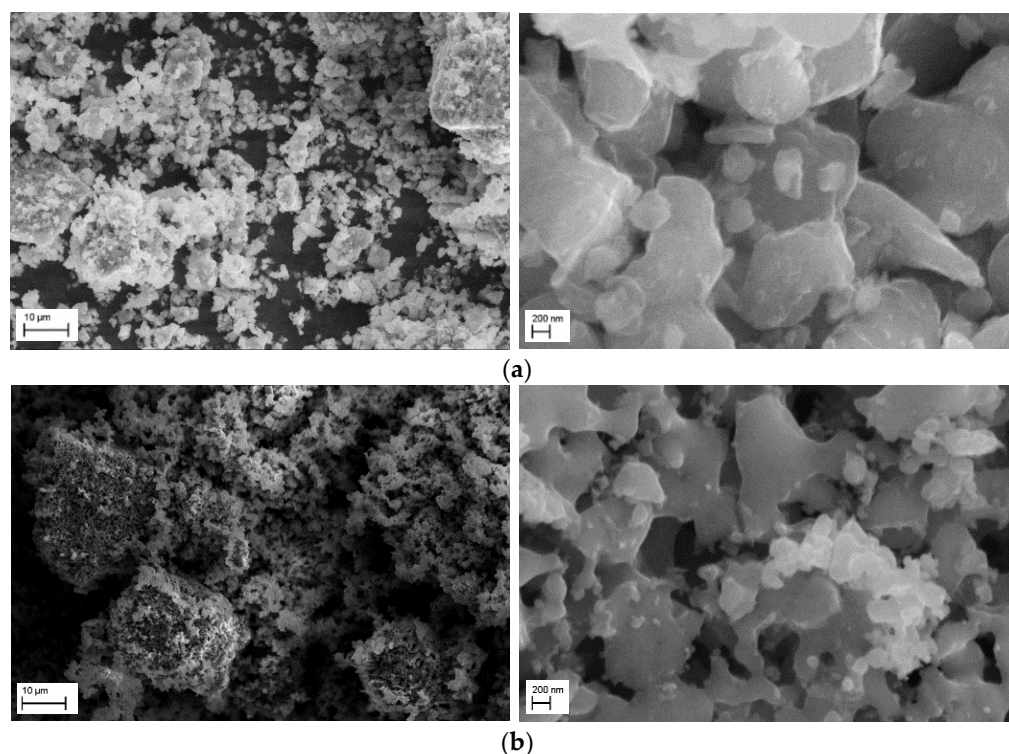


Figure 2. SEM images of the as-prepared (a) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (92.5 wt%)/ Li_3PO_4 (7.5 wt%) and (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (86 wt%)/ Li_3PO_4 (14 wt%) composites surface at different magnifications.

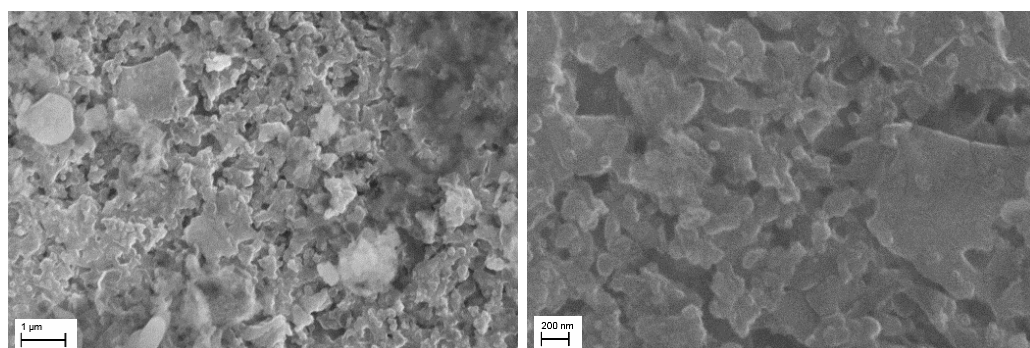


Figure 3. SEM images of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (86 wt%)/ Li_3PO_4 (14 wt%) composite surfaces after 200 charge/discharge cycles at different magnifications.

2.2. Electron Spin Resonance

Electron spin resonance (ESR) spectra of the LVPO/LPO-7.5 and LVPO/LPO-14 composites were measured on an ER 200 SRC (EMX/plus) spectrometer (Bruker, Bremen, Germany) at the frequency of 9.4 GHz and at room temperature using a double rectangular X-band resonator, ER 4105DR. This equipment allows detecting the electron spin resonance spectrum of the investigated sample and the benchmark spectrum simultaneously. The experimentally observed ESR spectra of the LVPO/LPO-7.5 and LVPO/LPO-14 composites at room temperature have a close line shape; the ESR spectrum of LVPO/LPO-14 is presented in Figure 5.

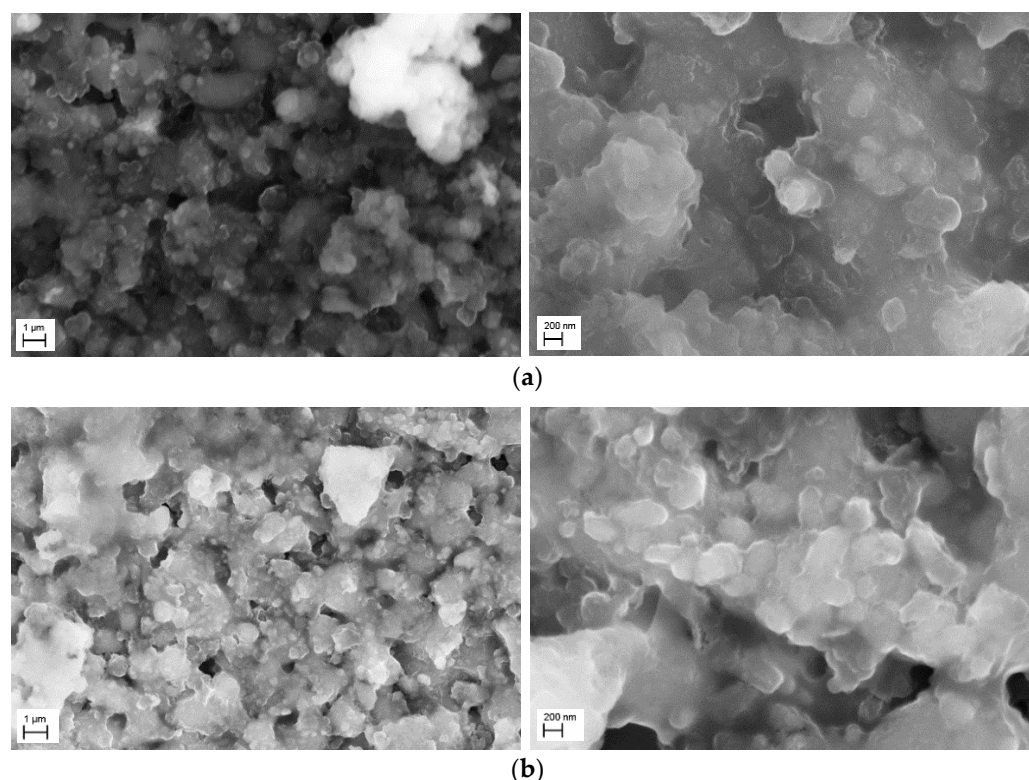


Figure 4. SEM images of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (92.5 wt%)/ Li_3PO_4 (7.5 wt%) composite surfaces after multiple charge/discharge cycles at different magnifications: (a) delithiated sample (b) relithiated sample.

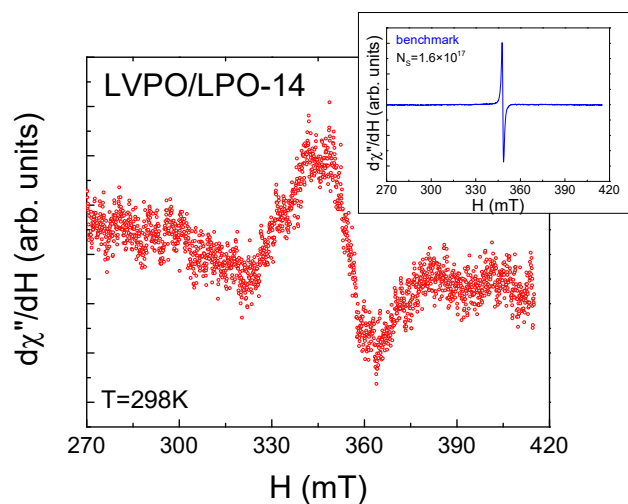


Figure 5. Electron resonance spectrum of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (86 wt%)/ Li_3PO_4 (14 wt%) composites at room temperature at the X-band frequency. Inset shows the electron spin resonance spectrum of the benchmark containing $N_s = 1.6 \times 10^{17}$ spins.

2.3. Electrochemical Performance

Electrochemical property investigations were performed by the galvanostatic method in a three-electrode electrochemical cell using a galvanostat/potentiostat PARSTAT 4000 (AMETEK Scientific Instruments, Berwyn, PA, USA). A $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ / Li_3PO_4 sample was used as working electrode; plates of metallic Li were used as reference and counter electrodes. A solution of LiPF_6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1.0 M LiPF_6 in EC/DMC = 50/50 (vol/vol)) was used as an electrolyte. All reagents were purchased from Sigma Aldrich and were “Battery grade”. The assembly of electrochemical cells was performed in a glovebox under a dry argon atmosphere. The oxygen content did

not exceed 1 ppm. The galvanostatic cycling tests and cycle characteristics were studied between the voltage window 2.5–4.5 V at room temperature.

Figures 6 and 7 show the electrochemical voltage profiles and the discharge capacity depending on the number of charge–discharge cycles at 1C, respectively, for the investigated LVPO/LPO-7.5 and LVPO/LPO-14 cathode materials.

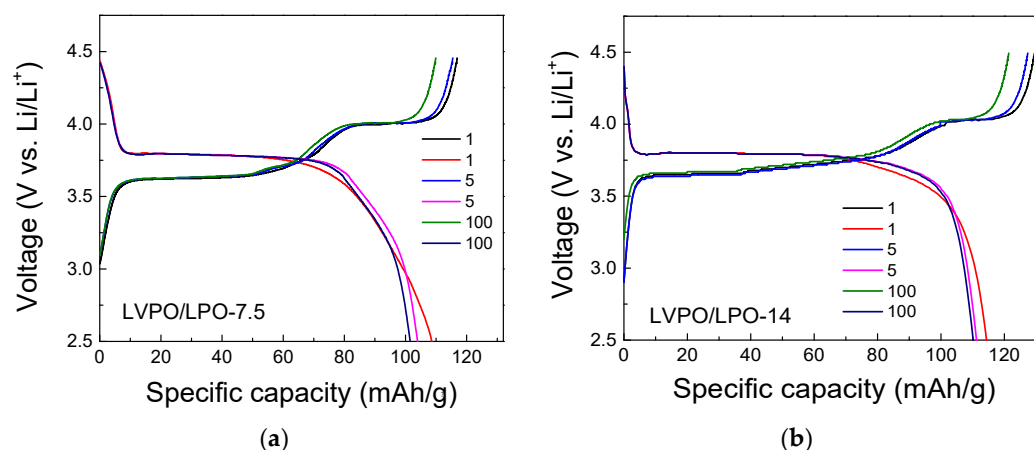


Figure 6. Electrochemical voltage profiles for (a) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (92.5 wt%)/ Li_3PO_4 (7.5wt%), (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (86 wt%)/ Li_3PO_4 (14 wt%) samples.

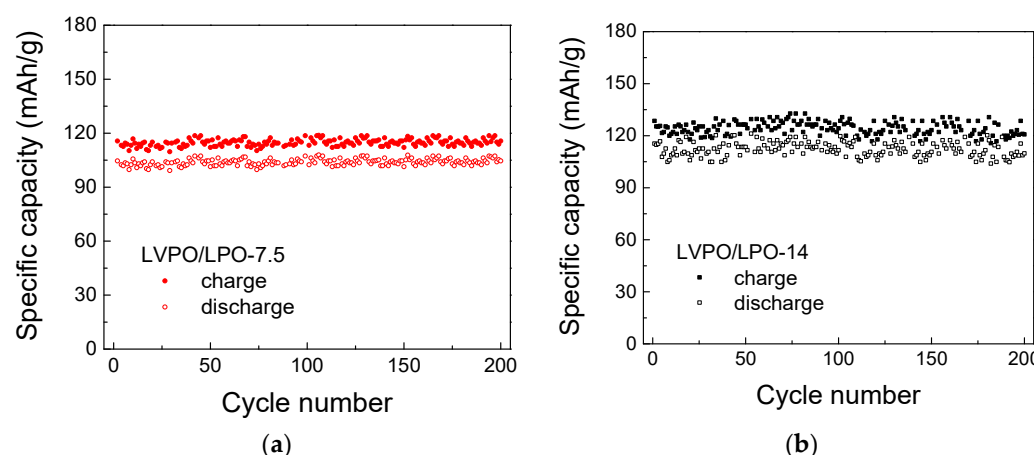


Figure 7. Long-term cycle performance at 1C up to 200 cycles in the voltage window 2.0–4.5 V for (a) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (92.5 wt%)/ Li_3PO_4 (7.5wt%), (b) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (86 wt%)/ Li_3PO_4 (14 wt%) samples.

3. Discussion

It is known from the literature that the lattice parameters can slightly differ depending on the synthesis process and monoclinic axis selection [16,22–27]. The here-observed difference between the crystal structure parameters of two investigated samples obtained by the same method lies within the error in determining the crystal structure parameters. From the SEM images, one can see that the as-prepared composites have a granular structure with closed values of the average grain sizes.

When discussing the nature of the signal, it is necessary to note that V^{3+} ($3d^2$, $S = 1$) has an even number of electrons in the respective electronic shells and singlet ground-state levels may result in such so that no ESR is observable. Thus, as it was suggested in our previous works [12,22], the observed ESR spectra is most probably due to a small amount of V^{4+} ions ($3d^1$, $S = 1/2$). To estimate the number of V^{4+} ions, the integral intensity of the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ spectrum was compared with the same parameters for the benchmark (inset Figure 5). The ESR spectra integral intensities ratio of the investigated samples ($I_{\text{LVPO/LPO}}$) and the benchmark (I_0) is given in Line 2 of Table 2. The corresponding number

of V^{4+} magnetic centers in the investigated samples can be estimated as $= I_{LVPO/LPO}/I_0 \cdot N_s$, where N_s is the spin number in the benchmark (Line 3 in Table 2); the total number of vanadium ions N_0 is given in Line 4 of Table 2. The relative number of tetravalent vanadium ions is shown in Line 5 of Table 2. The change in the valence state of vanadium ions from V^{3+} to V^{4+} can be associated with the lithium non-stoichiometry or anti-site defects (the occupation of V sites by Li and vice versa) in the investigated compound; that is, to maintain the electrochemical neutrality of the unit cell, the change in valence of one vanadium ion from 3+ to 4+ corresponds to the deintercalation of one lithium ion. Taking into account the vanadium to lithium ratio in the chemical formula, it is possible to estimate the degree of lithium nonstoichiometry in the investigated samples (Line 6 of Table 2).

Table 2. ESR spectra integral intensity ratio $I_{LVPO/LPO}/I_0$, number of magnetic centers, total number of vanadium ions, relative number of tetravalent vanadium ions and lithium deficiency for $Li_3V_2(PO_4)_3/Li_3PO_4$ composites.

No	Sample	LVPO/LPO-7.5	LVPO/LPO-14
1	mass (mg)	4.7	2.5
2	$I_{LVPO/LPO}/I_0$	4.813	8.355
3		7.7×10^{17}	1×10^{18}
4		12.83×10^{18}	6.34×10^{18}
5		6%	15.8%
6	lithium deficiency	4%	10.5%

One can see from Table 2 that the increase in the Li_3PO_4 content in LVPO/LPO composites leads to the decrease in the Li stoichiometry. Moreover, our previous results demonstrated the appearance of the magnetic inhomogeneity in LVPO/LPO-7.5 samples due to the Li nonstoichiometry [22]. Thus, one can expect an increase in the degree of magnetic inhomogeneity in the LVPO/LPO-14 sample with respect to the LVPO/LPO-7.5 sample, which can affect (improve) the electrochemical properties.

Traditionally, upon cycling in this voltage window, the curves for voltage profiles can be divided into three regions. These regions span the following composition ranges: $x = 0-0.5$, $0.5-1$, and $1-2$ in $Li_{3-x}V_2(PO_4)_3$, respectively. The removal of all three lithium ions is accompanied by redox reactions $V^{3+}/V^{4+}/V^{5+}$. In our case, we observed that the first two lithiums were extracted at an average voltage of 3.6 and 4.1 V vs. Li/Li^+ , respectively. The extraction of the third lithium associated with the V^{4+}/V^{5+} redox couple usually occurs at potentials higher than 4.5 V vs. Li/Li^+ to form $Li_0V_2(PO_4)_3$, in which transition metal V is in a mixed valance state of V^{4+} and V^{5+} and is not shown in the figure. The obtained discharge capacity was lower than the theoretical value (197 mAh/g for 3 Li extraction) [4,28,29]. One can suppose that such a behavior could be due to the presence of an additional phase that affects the electrochemical properties of the investigated samples and that leads to a decrease in the specific capacity. It can be seen from Figures 6 and 7 that the specific capacity is 10% higher for the sample with a higher lithium nonstoichiometry (with a high content of the Li_3PO_4 salt). The obtained results also show that the $Li_3V_2(PO_4)_3/Li_3PO_4$ composites demonstrate a lower initial specific charge–discharge capacity compared to $Li_3V_2(PO_4)_3/C$, however, at the same time, they retain their specific capacity during multiple cycling (up to 200 cycles), whereas for the $Li_3V_2(PO_4)_3/C$ sample, the specific capacity value can be maintained [7] or decreased by tens of percentage points even after 25 cycles [30].

One can see the retention of the granular structure after multiple intercalation/deintercalation processes accompanied by the visual compression and surface leveling (see Figures 2 and 3) which does not affect the electrochemical properties (see the values of the specific capacity in Figure 7). The surface morphology for different stages of electrochemical investigations is shown in Figure 4. One can see no visual difference between the delithiated and relithiated samples, which corresponds to the charge and discharge stages of the electrochemical cell.

4. Conclusions

$\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{Li}_3\text{PO}_4$ composites, containing 7.5 wt% and 14 wt% of Li_3PO_4 , were synthesized by the hydrothermal method and then subsequently annealed in an Ar atmosphere. No effect of Li_3PO_4 amount on the surface morphology of the investigated samples was observed; scanning electron microscopy measurements showed that the as-prepared samples had the granular structure and retained it after multiple intercalation/deintercalation processes, accompanied by visual compression and surface leveling. No visual difference between the surface morphology of delithiated and relithiated samples was observed.

At the same time, the effect of Li_3PO_4 content on the magnetic properties was detected. Using electron spin resonance, it was observed that there was a decrease in the Li stoichiometry with increasing Li_3PO_4 content in LVPO/LPO composites. From the point of view of the electrochemical properties, the increase in Li_3PO_4 content led to the increase of the discharge capacity: 105 and 120 mAh g^{-1} for the 200th cycle at 1C for LVPO/LPO-7.5 and LVPO/LPO-14, respectively, while the good cycle performance was realized for both samples.

We suggest that the improvement in the electrochemical performance of LVPO/LPO composites due to the incorporation of Li_3PO_4 can be attributed simultaneously to the chemical and magnetic inhomogeneity of the samples or just to one of these reasons, which requires further investigation.

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