β-NaVP2O7 as a Superior Electrode Material for Na-Ion Batteries

Oleg Drozhzhin, Ilya Tertov, Anastasia Alekseeva, Dmitry A. Aksyonov, Keith Stevenson, Artem M. Abakumov, Evgeny Antipov

Submitted date: 30/05/2019 • Posted date: 31/05/2019
Licence: CC BY-NC-ND 4.0
Citation information: Drozhzhin, Oleg; Tertov, Ilya; Alekseeva, Anastasia; Aksyonov, Dmitry A.; Stevenson, Keith; Abakumov, Artem M.; et al. (2019): β-NaVP2O7 as a Superior Electrode Material for Na-Ion Batteries. ChemRxiv. Preprint.

Herein, we present a novel β-polymorph of sodium vanadium pyrophosphate NaVP₂O₇ with the KAlP₂O₇-type structure obtained via hydrothermal synthesis and further thermal dehydration of a hydrophosphate intermediate. β-NaVP₂O₇ demonstrates attractive electrochemical behavior as a Na-ion positive electrode (cathode) material with practically achieved reversible capacity of 104 mAh/g at C/10 current density, average operating voltage of 3.9 V vs. Na/Na⁺ and only 0.5% volume change between the charged and discharged states. Electrode material exhibits excellent C-rate capability and cycling stability, providing the capacity of 90 mAh/g at 20C discharge rate and < 1% capacity loss after 100 charge-discharge cycles. At low voltage region (≈1.5 V vs. Na/Na⁺), β-NaVP₂O₇ reversibly intercalates additional sodium cations leading to unprecedented overall Na-ion storage ability exceeding 250 mAh/g within the 1.5 – 4.4 V vs. Na/Na⁺ voltage region. This material is one of only a few materials that exhibits reversible sodium ion storage capabilities over such a large potential window.

File list (2)

- article_NaVP2O7.pdf (2.51 MiB)
- SI_article_NaVP2O7.pdf (497.90 KiB)
$\beta$-NaVP$_2$O$_7$ as a superior electrode material for Na-ion batteries

Oleg A. Drozhzhin $^{1,2,3,*}$, Ilya V. Tertov$^1$, Anastasia M. Alekseeva$^1$, Dmitry A. Aksyonov$^2$, Keith J. Stevenson$^{2,3}$, Artem M. Abakumov$^{2,3}$, Evgeny V. Antipov$^{1,2,3}$

$^1$Department of Chemistry, Moscow State University, 119991, Moscow, Russia.
$^2$Skolkovo Institute of Science and Technology, 143026, Moscow, Russia
$^3$NTI Competence Center “Novel and mobile energy sources”.

*corresponding author. E-mail: o.drozhzhin@skoltech.ru

Abstract

Feasibility of sodium-ion batteries as an alternative to lithium-ion batteries in large-scale storage systems largely depends on availability of advanced electrode materials leading to enhanced energy density and operational sustainability. Herein, we present a novel $\beta$-polymorph of sodium vanadium pyrophosphate NaVP$_2$O$_7$ with the KAlP$_2$O$_7$-type structure obtained via hydrothermal synthesis and further thermal dehydration of a hydrophosphate intermediate. $\beta$-NaVP$_2$O$_7$ demonstrates attractive electrochemical behavior as a Na-ion positive electrode (cathode) material with practically achieved reversible capacity of 104 mAh/g at C/10 current density, average operating voltage of 3.9 V vs. Na/Na$^+$ and only 0.5% volume change between the charged and discharged states. Electrode material exhibits excellent C-rate capability and cycling stability, providing the capacity of 90 mAh/g at 20C discharge rate and < 1% capacity loss after 100 charge-discharge cycles. At low voltage region ($\approx$1.5 V vs. Na/Na$^+$), $\beta$-NaVP$_2$O$_7$ reversibly intercalates additional sodium cations leading to unprecedented overall Na-ion storage ability exceeding 250 mAh/g within the 1.5 – 4.4 V vs. Na/Na$^+$ voltage region. This material is one of only a few materials that exhibits reversible sodium ion storage capabilities over such a large potential window.

1. Introduction

The great interest of Na-ion batteries (SIB) as a more sustainable alternative to the already matured Li-ion technology promotes intensive search for novel electroactive materials for both positive (cathode) and negative (anode) electrode materials. Similar to the Li-ion intercalation systems, the oxide and polyanion materials are extensively scrutinized as potential cathodes with the aim to enhance the specific energy, durability and rate capability [1,2]. Whereas the layered oxides are characterized by greater volumetric energy density, the polyanion materials (typically phosphates and sulfates) usually exhibit better cycling and thermal stability and higher C-rate capability. Compared to the oxide structures based on close-packed
arrangement of the oxygen atoms, the polyanion compounds demonstrate an extra dimension in their crystal chemistry which significantly expands the search space for the materials with better electrochemical performance. Here we refer to the well-known tendency of polyanion compounds to form numerous polymorphs (although this trend is to some degree present in the oxide materials too, see, for instance, α- and β-forms of NaMnO₂ [3]). In various polymorphic forms the migration (diffusion) barriers for alkali cations can vary substantially depending on the shape and size of the transport tunnels in the framework built up by transition metal oxygen polyhedra and polyanions adopting different connectivity modes, which in turn can influence the redox (de)intercalation potential. Soft chemistry approaches play particularly important role in finding the hitherto unknown polymorphic forms as many of them can be “kinetically” stabilized at relatively mild conditions only or even appear to be metastable. The remarkable difference in electrochemical parameters between different polymorphs is illustrated by LiFeSO₄F tavorite/triplite, where the latter demonstrates the redox potential of the Fe²⁺/Fe³⁺ pair to be ~0.3 V higher compared to that in the former [4,5], NaFePO₄ maricite/triphylite, where only the latter is electrochemically active in the Na-ion cells [6], Na₂CoP₂O₇ orthorhombic/tetragonal/triclinic polymorphs, where only the layered orthorohombic phase shows reversible Na⁺ intercalation [7]; this list is by far not exhaustive.

In this work we have exploited the soft chemistry approach to look for the hitherto unknown electroactive polymorphs in sodium vanadium pyrophosphate NaVP₂O₇. Its monoclinic NaMoP₂O₇-structured form [8] has been reported as a cathode material with relatively poor electrochemical activity demonstrating the capacity of ~40 mAh/g (37% of the theoretical one) only at 3.4 V vs. Na/Na⁺ [9]. It’s worth noting that KVP₂O₇ [10] exhibits better electrochemical behavior in K-ion cell, showing reversible extraction/insertion of 0.6 K per f.u.(~ 60 mAh/g) with much higher working potential ~4.2 V vs. K/K⁺ [11]. However, the KAIP₂O₇-type structure is characteristic of pyrophosphates with large alkali cations, such as Rb or Cs [12], but it was not yet reported for Li or Na. Here, we present a synthetic route enabling stabilization of NaVP₂O₇ with the KAIP₂O₇ structure type. This new β-polymorph exhibits outstanding electrochemical performance as both positive and negative electrodes for Na-ion batteries.

2. Experimental section

2.1. Synthesis of β-NaVP₂O₇ powder. β-NaVP₂O₇ is prepared via two-step route. First, the NaV(HPO₄)₂ precursor was obtained via hydrothermal treatment of water solution of VOSO₄, NaOH and H₃PO₄ and hydrasinium sulfate N₂H₆SO₄ as a reducing agent in a stainless steel-lined PTFE reactor at 230°C for 24 h with continuous stirring. The resulting product was thoroughly
washed, dried in air and then annealed with addition of glucose (20 wt.%) as a carbon source at 600°C under Ar flow.

2.2. Materials characterization. The phase compositions of the obtained samples were characterized by powder X-ray diffraction (PXRD, Huber Guinier Camera G670, CuKα1 radiation, λ = 1.5406 Å). Particle size, morphology and cationic composition were investigated using a JEOL JSM-6490LV scanning electron microscope equipped with EDX spectrometer INCA X-Sight (Oxford Instruments). Thermogravimetric (TG) analysis was performed with a Netzsch STA 449 F1 Jupiter (Netzsch Gerätebau GmbH, Selb, Germany) at 5 K/min heating rate within 25-800°C temperature range under Ar atmosphere. Electron energy loss (EELS) spectra were obtained in a scanning transmission electron microscopy (STEM-EELS) mode with a FEI Titan G3 electron microscope operated at 120 kV and equipped with a monochromator and a Gatan Enfinium ER spectrometer. Energy resolution measured by full width at half maximum of the zero loss peak is 0.175 eV. The sample for the EELS measurements was prepared by crushing the crystals in a mortar in anhydrous ethanol and depositing drops of the suspension onto holey carbon grids.

2.3. DFT calculations. All DFT calculations were performed in VASP program [13] using generalized gradient approximation (GGA) to exchange-correlation functional and standard PAW PBE potentials [14] with minimum number of valence electrons. Gaussian smearing with smearing width of 0.1 eV was used for Brillouin-zone integrations. The energy cut-off was fixed at 400 eV. For α- and β-NaVP2O7 the 88 atom supercell and gamma-centered k-point 3x3x2 were used. To eliminate Pulay errors the lattice optimization (ISIF = 4) was performed at constant volume for several contracted and expanded cells (7 points). The migration barriers were determined using nudged elastic band (NEB) method as implemented in VASP using the unit cell. The method allows finding minimum energy path, which includes several intermediate configurations (images) between initial and final states. Five intermediate images were used. The optimization of atomic positions was performed using quasi-Newton algorithm until the maximum force permitted for any vector component was less than 0.1 eV/Å. The computational setup, including errors due to the periodic boundary conditions has been estimated to provide the precision of 0.1 eV for migration barriers.

2.4. Electrochemical testing. Electrode composite was prepared by mixing 75 wt.% of active compound, 12.5% of carbon black and 12.5% of PVDF binder in N-methylpyrrolidone and spreading it on an aluminum foil by doctor blade technique. Dried electrodes were rolled, punched to round discs and dried at 110°C for 3 h under dynamic vacuum. Two-electrode coin-
type cells were assembled in argon-filled glove-box (MBraun). Sodium metal was used as counter electrode, 1M solution of NaPF₆ in a 1:1 mixture of EC:PC was used as electrolyte. Galvanostatic study and cycling voltammetry were carried out using an Elins P-20X8 potentiostat-galvanostat (ES8 software). PXRD in operando regime was performed using a home-made electrochemical cell with Be windows at Huber G670 Guinier diffractometer.

3. Results and discussion

3.1. Material characterization. β-NaVP₂O₇ was prepared via thermal decomposition of the hydrothermally prepared precursor, which was identified as NaV(HPO₄)₂ [15]. Annealing at 600°C in Ar flow results in a new monoclinic phase with the unit cell parameters \(a = 7.1142(7)\) Å, \(b = 10.0709(7)\) Å, \(c = 8.0816(6)\) Å, \(\beta = 109.091(9)^{\circ}\), \(V = 547.16(8)\) Å³ and \(P2_1/c\) space group (Fig. 1a). Close similarity of the powder X-ray diffraction (PXRD) pattern of the new phase to that of KAlP₂O₇ [10] reflects their isostructural relationships. The annealed sample consists of large (~20-50 µm) aggregates comprising relatively small (~1 µm) irregular-shaped particles, as shown by scanning electron microscopy (SEM, Fig. 1b). Energy dispersive X-ray (EDX) analysis reveals the Na:V:P = 1:0.95:2.0 (±5% accuracy) cation ratio. Electron energy loss spectroscopy (EELS, Fig. 1c) demonstrates sharp V L₂,₃ edge with the onset at 513.2 eV with the shape very similar to that of V L₂,₃ edge in V₂O₅ confirming the formal oxidation state of +3 for V cations. Thermogravimetry performed for the as-prepared NaV(HPO₄)₂ under Ar atmosphere demonstrates 6.7% weight loss starting at 276 °C (Fig. S1 of Supporting information) pointing to the following decomposition reaction (calculated weight loss of 6.8 wt.%):

\[
\text{NaV(HPO}_4\text{)}_2 \rightarrow \text{NaVP}_2\text{O}_7 + \text{H}_2\text{O}
\]

These data strongly suggest that the new NaVP₂O₇ polymorph with the KAlP₂O₇-type structure has been obtained. Thus we denote the already known NaMoP₂O₇-structured polymorph as the α-phase, and the KAlP₂O₇-structured polymorph as the β-phase.
This conjecture was directly confirmed by the Rietveld refinement of the $\beta$-NaVP$_2$O$_7$ crystal structure (Fig. 1a, Tables S1, S2 of Supporting Information). It can be described as 3D framework formed by VO$_6$ octahedra and P$_2$O$_7$ tetrahedral pyrophosphate groups (Fig. 2a, b). Different framework geometry of $\alpha$- and $\beta$-NaVP$_2$O$_7$ structures provides significant difference in the Na$^+$ coordination environment (Fig. 2). Channels in $\beta$-NaVP$_2$O$_7$ are extended along the [001] and [110] directions and filled with sodium (Fig. 2a and 2b). The percolating migration of Na vacancy along [110] requires two different hops with distances of 4.54 Å and 8.51 Å. Due to too large distance of the latter hop we focused on [001] direction, in which percolating diffusion requires two hops with almost equal distances of 4.12 Å. According to the DFT calculations the corresponding migration barriers are 0.25 eV and 0.17 eV. The analysis of local coordination on the course of Na vacancy migration shows that surrounding oxygen displacements are minimal (Fig.2c) explaining quite low value of barrier [16]. Interestingly, after full deintercalation of Na from $\beta$-NaVP$_2$O$_7$ the barrier for Na migration along [001] even slightly reduces to 0.2 eV, which is highly important for exploiting full theoretical capacity of material. The obtained migration barriers are lower than that in a number of oxide and polyanion compounds [16], suggesting that $\beta$-NaVP$_2$O$_7$ can be used for efficient high-rate cathodes.

Switching to $\alpha$-NaVP$_2$O$_7$ the diffusion channels are arranged along the [110] and [101] directions (Fig. 2d and 2e). The percolating migration along [110] consists of two hops with 5.37 Å and 5.72 Å distances. The DFT calculated barrier for these hops are 0.85 eV, which is already
prohibitive for efficient diffusion. The migration along [101] also requires two hops: 4.12 Å and 5.68 Å with migration barriers of 0.5 eV and 2.6 eV, respectively, making [101] direction completely irrelevant for diffusion. The analysis of local coordination on the course of Na migration in α-NaVP₂O₇ shows that even in the case of 4.12 Å hop the displacements of surrounding oxygen are much more pronounced compared to β-NaVP₂O₇ (Fig. 2f). Taking into account exponential dependence of diffusion coefficient from migration barrier the diffusion of Na in α-NaVP₂O₇ should be by several orders of magnitude slower than that in β-NaVP₂O₇.

**Figure 2.** Crystal structure of β-NaVP₂O₇ viewed along the [001] and [110] directions (a, b) and α-NaVP₂O₇ along the [110] and [101] directions (d, e). Schematic representation of Na⁺ local coordination in the β- and α-phases is shown below each projection (red, green and blue “semi-bonds” correspond to O, P and V atoms, respectively). Overlapped Na⁺ positions from every image obtained from optimization with NEB method for shortest migration pathways in c) β-NaVP₂O₇, and f) α-NaVP₂O₇ structures.

### 3.2. Electrochemical properties of β-NaVP₂O₇ as a cathode material

Cyclic voltammetry (CV) measurements (Fig. 3a) as well as galvanostatic charge-discharge at low current (Fig. 3b) density reveal rather high potential of Na⁺ (de)intercalation in β-NaVP₂O₇. Oxidation of V³⁺ occurs at average potential of ≈ 4.15 V vs. Na/Na⁺, which is one of the highest values for the V³⁺/V⁴⁺ redox pair among Na-ion battery cathodes and higher than those in vanadium-based
fluorophosphates [17]. In general, (de)intercalation potential in sodium vanadium pyrophosphate varies from ≈3.5 V vs. Na/Na\(^{+}\) for $\alpha$-NaVP\(_2\)O\(_7\) to ≈4.1 V vs. Na/Na\(^{+}\) for recently reported Na\(_7\)V\(_3\)(P\(_2\)O\(_7\))\(_4\) cathode material [18].

Reduction of $\beta$-Na\(_{1-x}\)VP\(_2\)O\(_7\) proceeds via two distinct voltage platoes at ≈ 4.1 and ≈3.8 V. Clear and reproducible from cycle to cycle asymmetry (see Fig. S2) between charge and discharge curves is observed, although two platoes with intermediate region at appr. 50% state of charge are seen during both Na\(^{+}\) deintercalation and insertion processes.

**Figure 3.** (a) CV measurement for $\beta$-NaVP\(_2\)O\(_7\) performed within 2.0 – 4.5 V vs. Na/Na\(^{+}\) region at 0.1 mV/s scan rate; (b) Galvanostatic charge-discharge curves for $\beta$-NaVP\(_2\)O\(_7\) collected at 10 mA/g current density between 2.0 and 4.4 V vs. Na/Na\(^{+}\); (c) discharge curves at C/10-50C current densities (1C = 108 mA/g); (d) cycling stability at C/5 – C/5 and 1C – 1C charge-discharge regimes (e) operando PXRD data collected during Na\(^{+}\) deintercalation from $\beta$-NaVP\(_2\)O\(_7\) between 3.0 - 4.4 V vs. Na/Na\(^{+}\); (f) transformation of initial $\beta$-NaVP\(_2\)O\(_7\) into the desodiated $\beta$-VP\(_2\)O\(_7\) crystal structure.

At low current density $\beta$-NaVP\(_2\)O\(_7\) demonstrates specific capacity of 104 mAh/g, corresponding to 96% of the theoretical value (108 mAh/g). Increasing discharge current rate leads to remarkably low capacity fading (Fig. 3c): even at 50C the material provides 77 mAh/g, indicating only 25% loss of the nominal storage capacity. Such attractive power characteristics are in good agreement with low Na\(^{+}\) migration barrier obtained by DFT calculations.

PXRD pattern obtained for the desodiated electrode (charge up to 4.4 V vs. Na/Na\(^{+}\) at C/20 rate with subsequent potentiostatic step) is similar to that of K\(_{1-x}\)VP\(_2\)O\(_7\) [11]. LeBail fitting of PXRD data for $\beta$-VP\(_2\)O\(_7\) provides the lattice parameters $a = 7.819(3)$ Å, $b = 6.147(2)$ Å, $c =$
6.133(2) Å, α = 105.28(3)°, β = 103.21(4)°, γ = 96.37(4)°, V = 272.2(2) Å³, corresponding to \(P\bar{T}\) space group. The unit cell vectors of the triclinic phase relate to those of the initial monoclinic cell as \(a_{\tau} = c_m\), \(b_{\tau} = 1/2(a_m + b_m)\), \(c_{\tau} = 1/2(a_m - b_m)\). Unit cell volume of the charged phase relates to initial one as \(\approx 1:2\). The refinement of \(\beta\)-VP\(_2\)O\(_7\) structure model was performed within a rigid body approximation where the geometry of the PO\(_4\) groups was fixed to a tetrahedron similar to phosphate tetrahedra in the Na\(_2\)FePO\(_4\)F structure [19]. Two PO\(_4\) tetrahedra were included into refinement as connecting with each other via a shared oxygen atom. All atomic positions were refined with a common atomic displacement parameter. Results of the structure refinement are given in Table S1, S4, S5. According to the refinement, sodium atoms were not found in the charged \(\beta\)-VP\(_2\)O\(_7\) structure (values of the residual electron density maxima do not exceed 0.4 e\(^{-}/\)Å\(^3\)). It can be speculated that sodium deintercalation from \(\beta\)-NaVP\(_2\)O\(_7\) leads to the shrinkage of the VO\(_6\) octahedron together with the change of the conformation of the P\(_2\)O\(_7\) bitetrahedral groups (Fig. 3f). As a result, the change of the polyanion framework geometry allows forming \(\beta\)-Na\(_{1-x}\)VP\(_2\)O\(_7\) structure characterized by the 3D system of the broad channels extended along \(a\), \(b\) and \(c\)-axes.

The \(P_{2_1}/c \rightarrow P\bar{T}\) symmetry reduction and the corresponding two-phase transition appears after the very beginning of the charge process, as indicated by \textit{operando} PXRD data collected during Na\(^+\) deintercalation (Figure 3e). The second stage of the Na\(^+\) deintercalation (“Na\(_{0.4}\)VP\(_2\)O\(_7\)-VP\(_2\)O\(_7\)” ) proceeds via solid solution mechanism characterized by weak shift of the PXRD peak positions, as clearly seen in Figure 3d for the 010 and 001 reflections of the triclinic phase. It is worth noting that monoclinic \(\beta\)-NaVP\(_2\)O\(_7\) phase reappears after discharge (see Fig. S3). Resulting volume change (\(V_{m}/V_{n}\)) is +0.5(1)% only, thus designating \(\beta\)-NaVP\(_2\)O\(_7\) as a “zero-strain material”. As a result, \(\beta\)-NaVP\(_2\)O\(_7\) is characterized by excellent cycling stability: capacity loss after 90 cycles at 1C charge and discharge rate is negligible (85 mAh/g at 100\(^{th}\) cycle vs. 86 mAh/g after 10 cycles at C/5 rate). In spite of rather high upper potential limit (4.4 V vs. Na/Na\(^+\)), Coulombic efficiency during cycling is close to unity (typically 98.6 - 98.9%, see Fig. 3d).

**3.3. Anode properties of \(\beta\)-NaVP\(_2\)O\(_7\) material and its overall Na-ion storage ability.** Besides high-voltage redox reaction, corresponding to the “NaVP\(_2\)O\(_7\) ↔ VP\(_2\)O\(_7\)” transition, a low-voltage process is also observed for \(\beta\)-NaVP\(_2\)O\(_7\). Galvanostatic cycling, as well as CV measurements collected between 1.0 and 4.4 V vs. Na/Na\(^+\) reveals quite unusual electrochemical behavior of \(\beta\)-NaVP\(_2\)O\(_7\) material (Fig. 4a and b). Charge collected during sodiation between 1.5 and 1.0 V corresponds to \(\approx 150\) mAh/g of the specific capacity, leading to almost 1.5 Na cations insertion into the \(\beta\)-NaVP\(_2\)O\(_7\) crystal structure. However, only \(\approx 90\) mAh/g is gained at low (\(\approx 1.5\) V)
potential during desodiation, and the rest ≈60 mAh/g are “distributed” between 1.5 and 4.0 V. Total capacity value which can be obtained by cycling within 1.0 and 4.4 V interval exceeds 250 mAh/g (≈2.4 Na⁺ per f.u.).

**Figure 4.** First galvanostatic charge-discharge curves for β-NaVP₂O₇ electrode collected at 10 mA/g current density between 1.0 and 4.4 V vs. Na/Na⁺ (a); CV measurement performed within 1.0 – 4.4 V vs. Na/Na⁺ region at 0.1 mV/s scan rate (b); second charge-discharge cycle collected between 1.0 and 2.5 V vs. Na/Na⁺ (c); operando PXRD data collected during Na⁺ intercalation and deintercalation between 3.0 -1.0 - 3.9 V vs. Na/Na⁺.

Due to significant asymmetry, reversible capacity value at “anode” potential window (1.0 – 2.5 V) is smaller, amounting to 93 mAh/g at 10 mA/g current rate. Average potential is ≈1.3 V vs. Na/Na⁺ at intercalation and ≈1.55 V at deintercalation (see Fig. 4c). Operando PXRD reveals asymmetrical but reversible phase transformation occurring at low voltage region with restoring initial β-NaVP₂O₇ reflections at 4V (before beginning of the high-voltage two-phase transition shown in Fig. 3e). However, unambiguous determination of the crystal structure of the fully sodiated phase (corresponding to ≈Na₂.₄VP₂O₇ composition) by ex situ laboratory PXRD is
difficult due to low symmetry of the structure. The PXRD pattern of the fully sodiated phase is best indexed in a triclinic unit cell with $a = 7.1428(4) \text{ Å}$, $b = 9.9877(8) \text{ Å}$, $c = 8.2334(3) \text{ Å}$, $\alpha = 90.653(5)^\circ$, $\beta = 107.821(4)^\circ$, $\gamma = 89.976(6)^\circ$, $V = 559.15(9)\text{Å}^3$. Combination of synchrotron, neutron and electron diffraction would be of great help to resolve this complex crystal structure.

It is worth noting that significant asymmetry between deintercalation and insertion processes is a recognized phenomenon which was observed in case of several energetically non-equivalent sodium or lithium positions [20-22] or several d-cations with different redox potentials [23,24]. Very similar voltage asymmetry at Na\textsuperscript{+} extraction and insertion was reported by G. Yan et al for Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{2}F\textsubscript{3} cathode material [25]. Although authors did not provide an unambiguous origin of such a phenomena, they proposed presence of two energetically unequal sodium positions that may be filled/emptied in a different way due to different sodium environments associated to different V\textsuperscript{(n+1)+}/V\textsuperscript{n+} redox couples. The reason of asymmetric behavior of β-NaVP\textsubscript{2}O\textsubscript{7} material should be studied in a separate work using operando synchrotron or neutron diffraction coupled with first-principles calculations.

To round off the analysis of the obtained results, we should compare β-NaVP\textsubscript{2}O\textsubscript{7} with other intensively studied Na-ion polyanion cathode materials. Theoretical energy density of β-NaVP\textsubscript{2}O\textsubscript{7} as a cathode is 421 Wh/kg (108 mAh/g \times 3.9 V), and 393 Wh/kg is achieved experimentally. This value exceed that for such materials as NaFePO\textsubscript{4} [6], Na\textsubscript{2}FePO\textsubscript{4}F [26], Na\textsubscript{2}Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} [27] or Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} [28]. Energy density of sodium vanadium fluoride phosphates like Na\textsubscript{1.5}VPO\textsubscript{4.8}F\textsubscript{0.7} [29] is higher (experimentally achieved ~420-450 Wh/g), however, β-NaVP\textsubscript{2}O\textsubscript{7} is characterized by much smaller volume change during charge/discharge (0.5 vs. 2.9%) and easy and scalable synthetic route. Moreover, β-VP\textsubscript{2}O\textsubscript{7} framework is able to intercalate at least 2.4 Na\textsuperscript{+} per f.u., providing 255 mAh/g capacity when cycling within extended voltage region (1.0-4.4 V vs. Na/Na\textsuperscript{+}). This may be used for further improvement and fine tuning of the cathode or anode properties of β-NaVP\textsubscript{2}O\textsubscript{7} by means of homo- or heterovalent substitution in dication or anion sublattice.

Conclusions.

We believe that β-NaVP\textsubscript{2}O\textsubscript{7} is a unique material discovering new horizons for Na-ion battery technology. Simple hydrothermal synthesis makes it possible to produce high-performance cathode material operating at 3.9 V vs. Na/Na\textsuperscript{+} with 104 mAh/g reversible capacity. Rigid polyanion framework enables fast Na\textsuperscript{+} diffusion and stable galvanostatic cycling with only 0.5% of volume change. Low Na\textsuperscript{+} migration barrier of 0.25 eV calculated by DFT is in a good accordance with excellent electrochemical performance at high C-rate. As an anode material, β-NaVP\textsubscript{2}O\textsubscript{7} is able to intercalate additional Na\textsuperscript{+} cations providing 93 mAh/g of reversible capacity.
with 1.5 V average potential and 255 mAh/g of the overall storage ability when cycling between 1.0 and 4.4 V. Comparison with other Na-ion phosphate-, sulphate- or fluoride phosphate-based cathode materials reveals a number of benefits making $\beta$-NaVP$_2$O$_7$ attractive for practical application.

**Acknowledgements.**
This work was supported by the Russian Science Foundation (grant No. 17-73-30006) and Lomonosov Moscow State University Program of Development.

**Supporting Information.**
Thermogravimetric measurements for the initial NaV(HPO$_4$)$_2$ sample; E-C curves for the 1st, 50th and 90th charge-discharge cycles of $\beta$-NaVP$_2$O$_7$ at 1C current density; PXRD data for the initial $\beta$-NaVP$_2$O$_7$ powder and electrode after galvanostatic cycling; experimental, calculated and difference PXRD data for the desodiated $\beta$-VP$_2$O$_7$ electrode; refinement details and crystal structure parameters for $\beta$-NaVP$_2$O$_7$ and $\beta$-VP$_2$O$_7$ phases. This material is available free of charge via the Internet at http://pubs.acs.org.
References

1. J.-Y. Hwang, S.-T. Myung and Y.-K. Sun, Sodium-ion batteries: present and future, Chem. Soc. Rev., 2017, 46, 3529-3614
2. K. Kubota, S. Komaba, Review—Practical Issues and Future Perspective for Na-Ion Batteries, Journal of The Electrochemical Society, 162 (14) A2538-A2550 (2015)
3. A.M. Abakumov, A.A. Tsirlin, I. Bakaimi, G. Van Tendeloo, A. Lappas, Multiple Twinning As a Structure Directing Mechanism in Layered Rock-Salt-Type Oxides: NaMnO₂ Polymorphism, Redox Potentials, and Magnetism, Chem. Mater., 26, 3306–3315 (2014)
4. P. Barpanda, M. Ati, B. C. Melot, G. Rousse, J-N. Chotard, M-L. Doublet, M. T. Sougrati, S. A. Corr, J-C. Jumas, J-M. Tarascon, A 3.90 V iron-based fluorosulphate material for lithium-ion batteries crystallizing in the triplite structure, Nature Mater., 10, 772-779 (2011)
5. M. Ati, M. Sathiya, S. Boulineau, M. Reynaud, A. Abakumov, G. Rousse, B. Melot, G. Van Tendeloo, J.-M. Tarascon, Understanding and Promoting the Rapid Preparation of the Triplite-Phase of LiFeSO₄F for Use as a Large-Potential Fe Cathode, J. Am. Chem. Soc. 134, 18380–18387 (2012)
6. N. Le Poul, E. Baudrin, M. Morcrette, S. Gwizdala, C. Masquelier, J.-M. Tarascon, Development of potentiometric ion sensors based on insertion materials as sensitive element, Solid State Ionics, 159, 149-158 (2003)
7. P. Barpanda, J. Lu, T. Ye, M. Kajiyama, S.-C. Chung, N. Yabuuchi, S. Komaba, A. Yamada, A layer-structured Na₂CoP₂O₇ pyrophosphate cathode for sodium-ion batteries, RSC Adv., 3, 3857-3860 (2013)
8. Y.P. Wang, K.H. Lii, S.L. Wang, Structure of NaVP₂O₇, Acta Crystallogr. C45 (1989) 1417-1418.
9. Y. Kee, N. Dimov, A. Staikov, P. Barpanda, Y.-C. Lu, K. Minamie, S. Okada, Insight into the limited electrochemical activity of NaVP₂O₇, RSC Adv., 2015,5, 64991
10. Ng, H.N.; Calvo, C. The crystal structure of KAlP₂O₇, Canadian Journal of Chemistry, 1973, 51, 2613-2620.
11. W. B. Park, S. C. Han, C. Park, S. U. Hong, U. Han, S. P. Singh, Y. H. Jung, D. Ahn, K.-S. Sohn, M. Pyo, KVP₂O₇ as a Robust High-Energy Cathode for Potassium-Ion Batteries: Pinpointed by a Full Screening of the Inorganic Registry under Specific Search Conditions Adv. Energy Mater. 2018, 8, 1703099.
12. Durif, A., Crystal Chemistry of Condensed Phosphates, Springer US, 1995
13. G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Comput. Mater. Sci. 6 (1), p. 15–50 (1996)
14. J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Phys. Rev. Lett. 77 (18), p. 3865–3868 (1996)
15. D.A. Rusakov, Synthesis, crystal structure and properties of the complex hydrophosphates $M^I(M^{II})$ and $M^{III}$ – cations ($M^{III} = Al, Ga, Fe, Sc и In$), Ph.D. thesis, Moscow, 2008
16. D.A. Aksyonov, S.S. Fedotov, K.J. Stevenson, A. Zhugayevych, Understanding migration barriers for monovalent ion insertion in transition metal oxide and phosphate based cathode materials: A DFT study, Computational Materials Science 154 (2018) 449–458
17. R.K.B.Gover, A.Bryan, P.Burns, J.Barker, The electrochemical insertion properties of sodium vanadium fluorophosphate, $Na_3V_2(PO_4)_2F_3$, Solid State Ionics, 177, 2006, pp. 1495-1500
18. J. Kim, I. Park, H. Kim, K.-Y. Park, Y.-U. Park, K. Kang, Tailoring a New 4V-Class Cathode Material for Na-Ion Batteries, Adv. Energy Mater. 2016, 6, 1502147
19. Ellis, B.L.; Makahnouk, W.R.M.; Rowan-Weetaluktuk, W.N.; Ryan, D.H.; Nazar, L.F. Crystal structures and electrochemical properties of $A_2MPO_4F$ fluorophosphates ($A = Na, Li; M = Fe, Mn, Co, Ni$), Chemistry of Materials (2010), 22(3), 1059-1070
20. Yin, S. C.; Grondey, H.; Strobel, P.; Anne, M.; Nazar, L. F. Electrochemical Property: Structure Relationships in Monoclinic $Li_{3.4}V_2(PO_4)_3$. J. Am. Chem. Soc. 2003, 125 (34), 10402–10411
21. M. V. Zakharkin, O. A. Drozhzhin, I. V. Tereshchenko, D. Chernyshov, A. M. Abakumov, E. V. Antipov, K. J. Stevenson, Enhancing Na$^+$ Extraction Limit through High Voltage Activation of the NASICON-Type $Na_4MnV(PO_4)_3$ Cathode, ACS Applied Energy Materials 2018 1 (11), 5842-5846
22. Chen, F.; Kovrugin, V. M.; David, R.; Mentré, O.; Fauth, F.; Chotard, J.-N.; Masquelier, C. A NASICON-Type Positive Electrode for Na Batteries with High Energy Density: $Na_4MnV(PO_4)_3$. Small Methods 2018, 2, 1800218.
23. Ravnsbæk, D. B.; Xiang, K.; Xing, W.; Borkiewicz, O. J.; Wiaderek, K. M.; Gionet, P.; Chapman, K. W.; Chupas, P. J.; Chiang, Y.-M. Extended Solid Solutions and Coherent Transformations in nanoscale Olivine Cathodes. Nano Lett., 14 (2014) 1484–1491.
24. Drozhzhin, O.A., Sumanov, V.D., Karakulina, O.M., Abakumov, A.M., Hadermann, J., Baranov, A.N., Stevenson, K.J., Antipov, E.V., Switching between solid solution and two-phase regimes in the $Li_{1-x}Fe_{1-y}Mn_3PO_4$ cathode materials during lithium
(de)insertion: Combined PITT, in situ XRPD and electron diffraction tomography study, (2016) ElectrochimicaActa, 191, pp. 149-157.

25. G. Yan, S. Mariyappan, G. Rousse, Q. Jacquet, M. Deschamps, R. David, B. Mirvaux, J. W. Freeland, J.-M. Tarascon, Higher energy and safer sodium ion batteries via an electrochemically made disordered Na$_3$V$_2$(PO$_4$)$_2$F$_3$ material, Nat. Commun., 10, Article number: 585 (2019)

26. Ellis, B. L.; Makahnouk, W. R. M.; Makimura, Y.; Toghill, K.; Nazar, L. F. A multifunctional 3.5 V iron-based phosphate cathode for rechargeable batteries. Nat. Mater., 6 (2007) 749 – 753

27. P. Barpanda, G. Oyama, S.-i. Nishimura, S.-C.Chung & A. Yamada, A 3.8-V earth-abundant sodium battery electrode, Nature Communications volume 5, Article number: 4358 (2014)

28. Saravanan, K.; Mason, C. W.; Rudola, A.; Wong, K. H.; Balaya, P. The First Report on Excellent Cycling Stability and Superior Rate Capability of Na$_3$V$_2$(PO$_4$)$_3$ for Sodium Ion Batteries. Adv. Energy Mater. 2013, 3 (4), 444–450

29. Y.-U. Park, D.-H. Seo, H.-S. Kwon, B. Kim, J. Kim, H. Kim, I. Kim, H.-I. Yoo, and K. Kang, A New High-Energy Cathode for a Na-Ion Battery with Ultrahigh Stability, J.Am. Chem. Soc. 2013 135 (37), 13870-13878
as a novel bifunctional Na-ion electrode material
Supporting Information for

$\beta$-NaVP$_2$O$_7$ as a superior electrode material for Na-ion batteries

Oleg A. Drozhzhin $^{1,2,3}*,$ Ilya V. Tertov$^1,$ Anastasia M. Alekseeva$^1,$ Dmitry A. Aksyonov$^2,$ Keith J. Stevenson$^{2,3},$ Artem M. Abakumov$^{2,3},$ Evgeny V. Antipov$^{1,2,3}$

$^1$Department of Chemistry, Moscow State University, 119991, Moscow, Russia.
$^2$Skolkovo Institute of Science and Technology, 143026, Moscow, Russia
$^3$NTI Competence Center “Novel and mobile energy sources”.

*corresponding author. E-mail: o.drozhzhin@skoltech.ru

**Figure S1.** TG and DSC data for the NaV(HPO$_4$)$_2$ precursor (Ar atmosphere, 5 K/min heating rate).

**Figure S2.** E-C curves for the 1$^{st}$, 50$^{th}$ and 90$^{th}$ charge-discharge cycles of $\beta$-NaVP$_2$O$_7$ at 1C current density.
Figure S3. PXRD data for the initial $\beta$-NaVP$_2$O$_7$ powder and electrode after galvanostatic cycling.

Figure S4. Experimental, calculated and difference PXRD data for the desodiated $\beta$-VP$_2$O$_7$ electrode.

Table S1. Data collection and crystallographic parameters for $\beta$-NaVP$_2$O$_7$ and $\beta$-VP$_2$O$_7$.

| Chemical composition         | NaVP$_2$O$_7$ | VP$_2$O$_7$  |
|------------------------------|---------------|--------------|
| Chemical formula weight      | 247.9         | 229.3        |
| Space group                  | $P2_1/c$      | $P\bar{1}$   |
| $a$, Å                       | 7.1142(7)     | 7.819(3)     |
| $b$, Å                       | 10.0709(7)    | 6.147(2)     |
| $c$, Å                       | 8.0816(6)     | 6.133(2)     |
| $\alpha$, $\beta$, $\gamma$, $^\circ$ | 90, 109.091(9), 90 | 105.28(3), 103.21(4), 96.37(4) |
| $V$, Å$^3$                   | 547.16(8)     | 272.2(2)     |
| $Z$                          | 4             | 2            |
Calculated density, g·cm\(^{-3}\) 3.00 2.80
Radiation \(\lambda\), Å CuK\(_\alpha\), 1.54056 CuK\(_\alpha\), 1.54056
20 range, ° 5.008–100.287 7.008–100.287
Absorption coefficient, cm\(^{-1}\) 21.868 21.3
Number of points 4765 4665
Number of observed reflections 562 560
Refined parameters 60 44
\(R_I, R_{exp}\) 0.022, 0.032 0.052, 0.076
\(R_p, R_{wp}\) 0.022, 0.028 0.029, 0.041
\(\chi^2\) 2.75 12.36

**Table S2.** Atomic coordinates and isotropic displacement parameters for \(\beta\)-NaVP\(_2\)O\(_7\).

| Atom | Site | \(x/a\) | \(y/b\) | \(z/c\) | \(U_{iso}\), Å\(^2\) |
|------|------|--------|--------|--------|----------------|
| Na   | 4e   | 0.851(3) | 0.182(1) | 0.429(2) | 0.072(7) |
| V    | 4e   | 0.2329(9) | 0.1021(7) | 0.2617(8) | 0.012(2) |
| P1   | 4e   | 0.144(2) | 0.404(1) | 0.328(1) | 0.018(3)\(^1\) |
| P2   | 4e   | 0.461(2) | 0.356(1) | 0.200(1) | 0.018(3) |
| O1   | 4e   | 0.138(3) | 0.401(2) | 0.514(3) | 0.009(2)\(^2\) |
| O2   | 4e   | 0.313(3) | 0.374(2) | 0.016(2) | 0.009(2) |
| O3   | 4e   | 0.011(3) | 0.515(2) | 0.214(2) | 0.009(2) |
| O4   | 4e   | 0.462(3) | 0.212(2) | 0.252(2) | 0.009(2) |
| O5   | 4e   | 0.673(2) | 0.421(2) | 0.233(3) | 0.009(2) |
| O6   | 4e   | 0.088(3) | 0.272(2) | 0.236(2) | 0.009(2) |
| O7   | 4e   | 0.365(3) | 0.430(2) | 0.327(2) | 0.009(2) |

\(^1\) Atomic displacement parameters for P1 and P2 atoms were constrained to be equal.

\(^2\) Atomic displacement parameters for all oxygen atoms were constrained to be equal.

**Table S3.** Selected interatomic distances in \(\beta\)-NaVP\(_2\)O\(_7\).

| Atoms | Distance, Å | Atoms | Distance, Å |
|-------|------------|-------|------------|
| Na–O1 | 2.93(2) | V–O1  | 1.89(2) |
| O3    | 2.42(3) | O2    | 1.96(2) |
| O3    | 2.97(2) | O3    | 2.01(2) |
| O4    | 2.69(2) | O4    | 1.99(2) |
| O5  | 2.93(2) | O5  | 1.94(2) |
|-----|---------|-----|---------|
| O6  | 2.80(3) | O6  | 1.97(2) |
| O6  | 2.54(2) |     |         |
| P–O1| 1.52(3) | P2–O2| 1.53(2) |
| O3  | 1.56(2) | O4  | 1.52(2) |
| O6  | 1.51(2) | O5  | 1.58(2) |
| O7  | 1.60(2) | O7  | 1.58(2) |

| Table S4. Atomic coordinates and isotropic displacement parameters for β-VP₂O₇ |
|---------------------------------------------------------------|
| **Atom** | **Site** | **x/a** | **y/b** | **z/c** | **Uᵦ, Å²** |
|-----------|----------|---------|---------|---------|-------------|
| V         | 2d       | 0.274(3)| 0.304(5)| 0.624(5)| 0.001(8)    |
| P1 ¹)     | 2d       | 0.289(4)| 0.451(5)| 0.188(5)| 0.03²)      |
| P2        | 2d       | 0.163(4)| 0.752(4)| 0.513(5)| 0.03        |
| O1        | 2d       | 0.46(4) | 0.62(4) | 0.22(1) | 0.03        |
| O2        | 2d       | 0.33(4) | 0.27(3) | 0.31(1) | 0.03        |
| O3        | 2d       | 0.21(1) | 0.33(1) | -0.08(1)| 0.03        |
| O4        | 2d       | -0.033(5)| 0.76(1)| 0.51(1) | 0.03        |
| O5        | 2d       | 0.247(8)| 0.63(1) | 0.68(1) | 0.03        |
| O6        | 2d       | 0.265(9)| 1.00(1) | 0.59(1) | 0.03        |
| O7        | 2d       | 0.17(1) | 0.63(1) | 0.261(8)| 0.03        |

¹) Atomic coordinates of P1, P2 and O1–O7 atoms were refined using the rigid body model consisting of two connected tetrahedra.

²) Displacement parameters for P1, P2 and O1–O7 atoms were fixed.

| Table S5. Selected interatomic distances in β-VP₂O₇. |
|---------------------------------------------------|
| **Atoms** | **Distance, Å** | **Atoms** | **Distance, Å** |
|-----------|-----------------|-----------|-----------------|
| V–O1      | 2.01(5)         | P1–O1     | 1.53(5)         |
| O2        | 2.01(3)         | O2        | 1.51(3)         |
| O3        | 1.97(1)         | O3        | 1.56(1)         |
| O4        | 1.83(1)         | O7        | 1.57(1)         |
| O5        | 1.97(1)         | P2–O4     | 1.53(1)         |
| O6        | 1.80(1)         | O5        | 1.51(1)         |
|           |                 | O6        | 1.56(1)         |
|           |                 | O7        | 1.55(1)         |
