Supporting Information for

β-$NaVP_2O_7$ as a superior electrode material for Na-ion batteries

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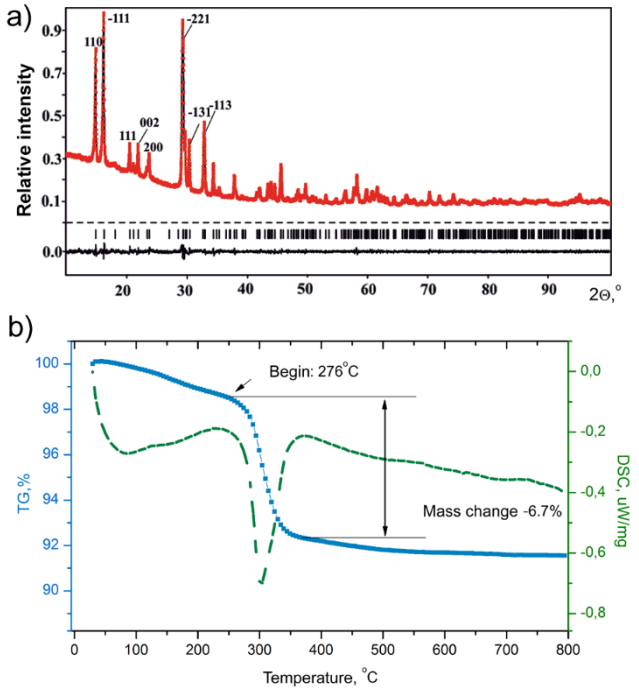

Figure S1. PXRD pattern of the initial $NaV(HPO_4)_2$ precursor (a) and TG and DSC data for the same material (Ar atmosphere, 5 K/min heating rate) (b).

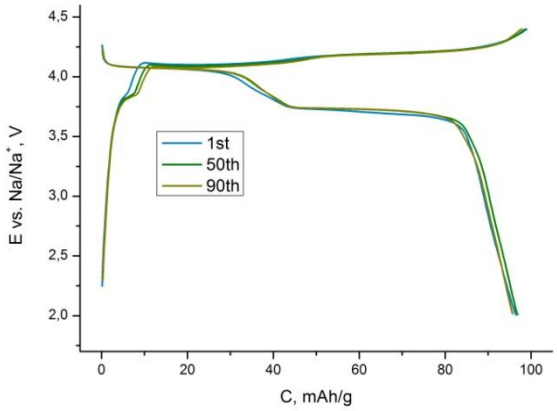

Figure S2. E-C curves for the 1st, 50th and 90th charge-discharge cycles of β-$NaVP_2O_7$at 1C current density.

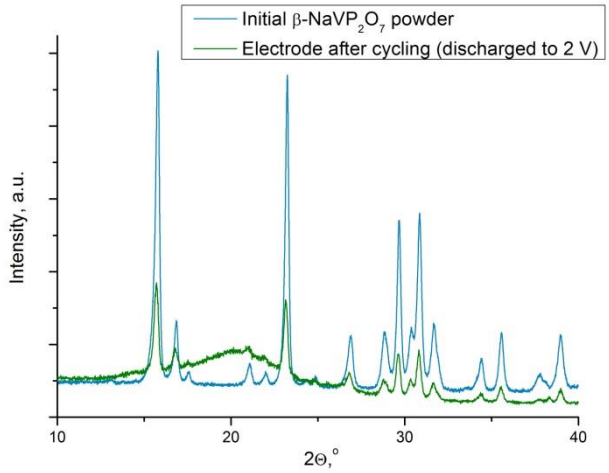

Figure S3. PXRD data for the initial β-$NaVP_2O_7$ powder and electrode after galvanostatic cycling.

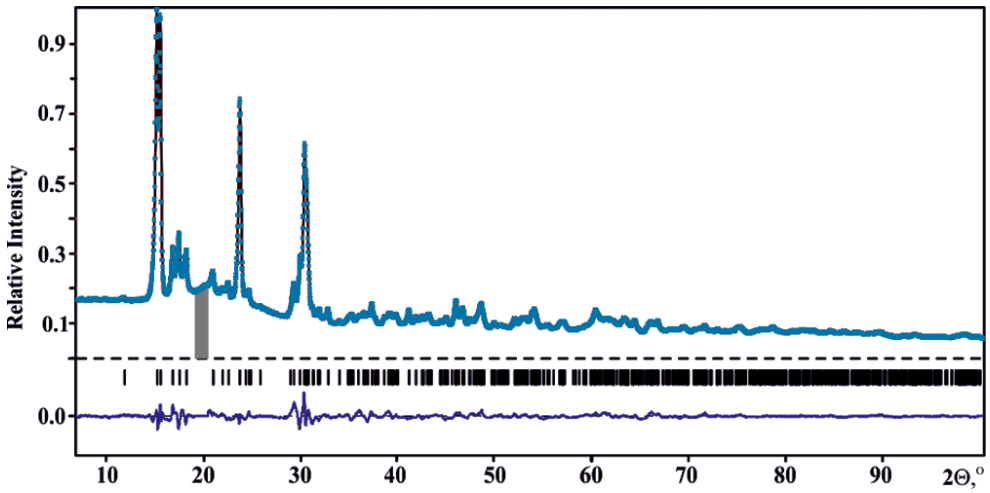

Figure S4. Experimental, calculated and difference PXRD data for the desodiated β-VP_2O_7 electrode.

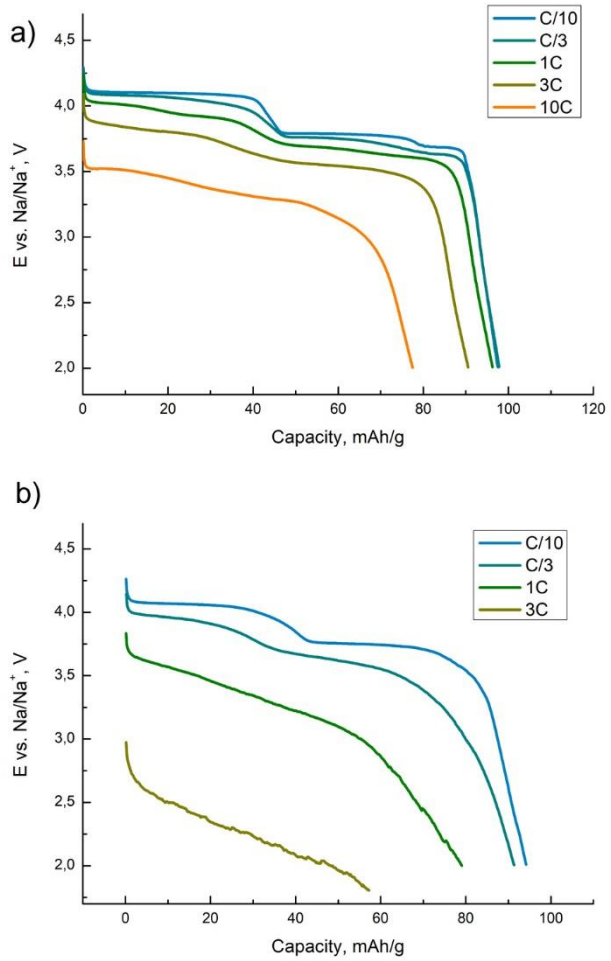

Figure S5. Discharge curves collected at different rates for the electrodes prepared with 85% (a) and 90% (b) loading of the β-$NaVP_2O_7$active material.

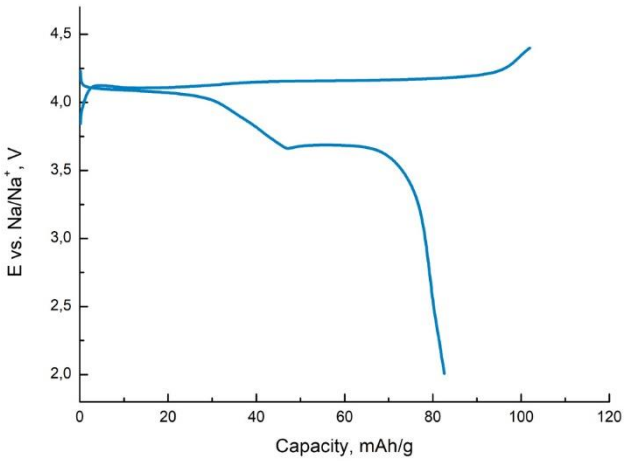

Figure S6. Charge-discharge curves collected at C/10 rate for the electrode prepared from β-$NaVP_2O_7$ annealed without carbon source (80% active material, 10% carbon black, 10% PVDF electrode composition).

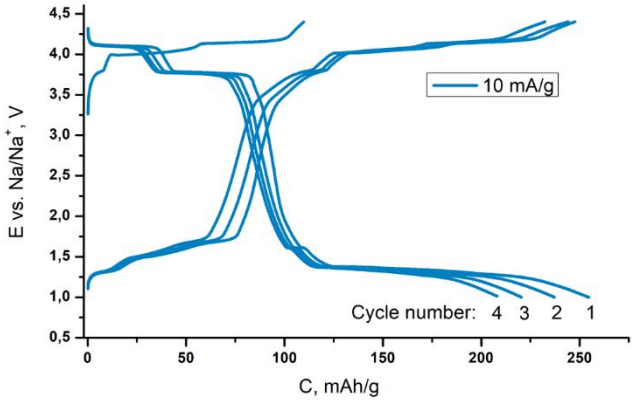

Figure S7. Charge-discharge curves obtained during galvanostatic cycling of the *β*-$NaVP_2O_7$material within 1.0-4.4 V vs. Na/Na^+potential window at 10 mA/g current density.

Table S1. Data collection and crystallographic parameters for *β*-$NaVP_2O_7$ and *β*-VP_2O_7.

Chemical composition	$NaVP_2O_7$	VP_2O_7
Chemical formula weight	247.9	224.9
Space group	$P2_1/c$	$P\bar{1}$
a, Å	7.1142(7)	7.819(3)
b, Å	10.0709(7)	6.147(3)
c, Å	8.0816(6)	6.133(2)
α, *β*, *γ*, °	90, 109.091(9), 90	105.28(3), 103.21(5), 96.37(5)
V,Å^3	547.16(8)	272.2(2)
Z	4	2
Calculated density, g·cm^{-3}	3.01	2.74
Radiation *λ*, Å	Cu*K*α, 1.54056	Cu*K*α, 1.54056
2θ range, °	5.008–100.287	7.008–100.287
Absorption coefficient, cm^{-1}	21.868	21.138
Number of points	4765	4665
Number of observed reflections	562	560
Refined parameters	60	44
R_I, R_{exp}	0.022, 0032	0.052, 0.076
R_p, R_{wp}	0.022, 0.028	0.030, 0.041
χ^2	2.76	12.51

Table S2. Atomic coordinates and isotropic displacement parameters for β-$NaVP_2O_7$

Atom	Site	*x/a*	*y/b*	*z/c*	U_{iso} , Å^2
Na	4*e*	0.851(3)	0.182(1)	0.430(2)	0.072(7)
V	4*e*	0.2329(9)	0.1022(7)	0.2617(8)	0.012(2)
P1	4*e*	0.144(2)	0.404(1)	0.328(1)	0.018(3)[1)]
P2	4*e*	0.461(2)	0.356(1)	0.200(1)	0.018(3)
O1	4*e*	0.138(3)	0.401(2)	0.514(3)	0.009(2)[2)]
O2	4*e*	0.313(3)	0.374(2)	0.016(2)	0.009(2)
O3	4*e*	0.011(3)	0.515(2)	0.214(2)	0.009(2)
O4	4*e*	0.462(3)	0.212(2)	0.252(2)	0.009(2)
O5	4*e*	0.673(2)	0.421(2)	0.233(3)	0.009(2)
O6	4*e*	0.088(3)	0.272(2)	0.236(2)	0.009(2)
O7	4*e*	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 β-$NaVP_2O_7$.

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)		
P1−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-VP_2O_7

Atom	Site	*x/a*	*y/b*	*z/c*	U_{iso} , Å^2
V	2*d*	0.274(3)	0.304(5)	0.624(5)	0.001(8)
P1[1)]	2*d*	0.289(4)	0.451(5)	0.188(5)	0.03[2)]
P2	2*d*	0.163(4)	0.752(4)	0.513(5)	0.03
O1	2*d*	0.46(4)	0.62(4)	0.22(1)	0.03
O2	2*d*	0.33(4)	0.27(3)	0.31(1)	0.03
O3	2*d*	0.21(1)	0.33(1)	-0.08(1)	0.03
O4	2*d*	-0.033(5)	0.76(1)	0.51(1)	0.03
O5	2*d*	0.247(8)	0.63(1)	0.68(1)	0.03
O6	2*d*	0.265(9)	1.00(1)	0.59(1)	0.03
O7	2*d*	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 inβ-VP_2O_7.

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)