Supporting Information for

Structure and Electrochemical Properties of $Na_{2\pm x}V_3P_2O_{13}$ (x = 0 and 1): A Promising Cathode Material for Sodium-Ion Batteries

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Table S1. Comparison of state-of-the-art cathode materials for NIBs

NIB cathode materials	Ave. Potential (V) *vs.* Na/Na^+	Sp. Capacity (mAh g^{-1})	Sp. Energy (Wh kg^{-1})
O3-$NaMn_{0.25}Fe_{0.5}Ni_{0.25}O_2$	3.0	140	420
P2- $Na_xMg_{0.11}Mn_{0.89}O_2$	3.0	148	444
P3/P2/O3-$Na_{0.76}Mn_{0.5}Ni_{0.3}Fe_{0.1}Mg_{0.1}O_2$	3.3	155	511
$Na_2Fe(PO_4)F$	3.0	100-124	300-372
$Na_3V_2(PO_4)_3$	3.4	117	397
$Na_3V_2(PO_4)_2F_3$	3.9	120	468
$Na_2Fe_2(SO_4)_3$	3.8	100-120	380-456

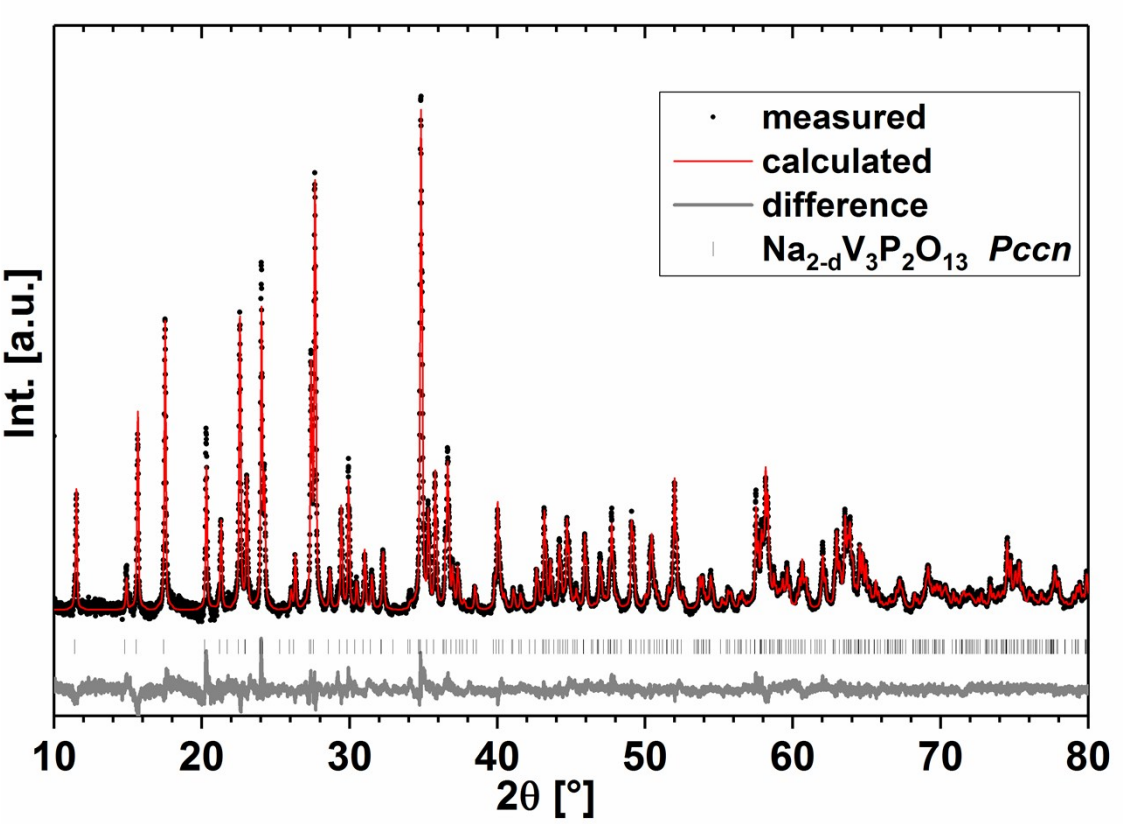

Figure S1. Rietveld analysis of powder XRD patterns recorded for $Na_{2-x}V_3P_2O_{13}$

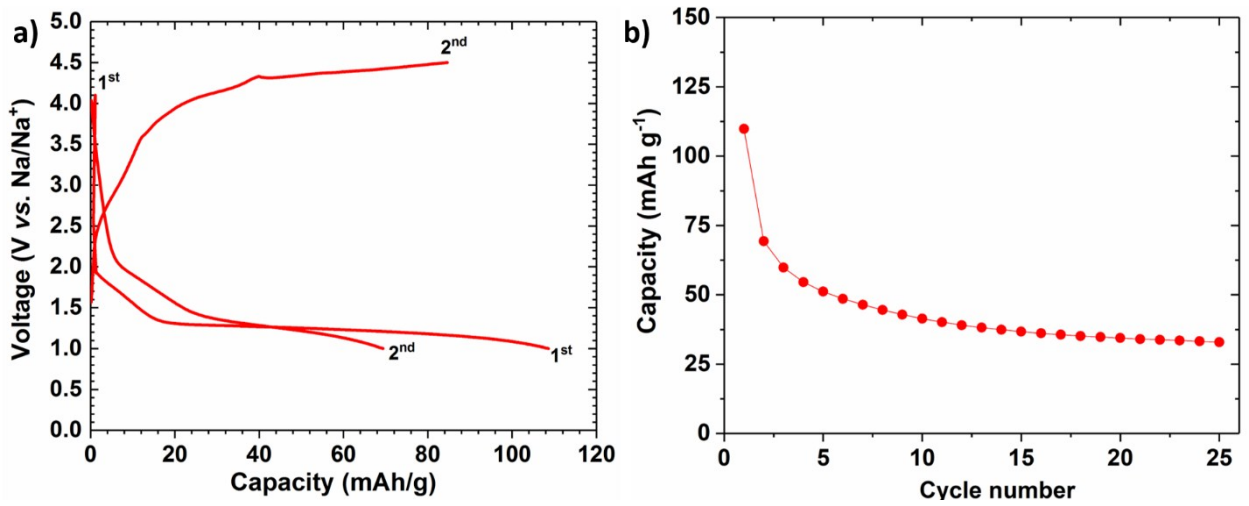

Figure S2 a) discharge and charge curves of as synthesized $Na_2V_3P_2O_{13}$ for the first two cycles, b) cycling bahviour of the same cell. The discharge-charge curves were obtained at 25 °C, at a current rate of C/20 and in the voltage window of 1.0-4.5 V *vs*. Na/Na^+. Capacities were calculated based on the weight of the active material.

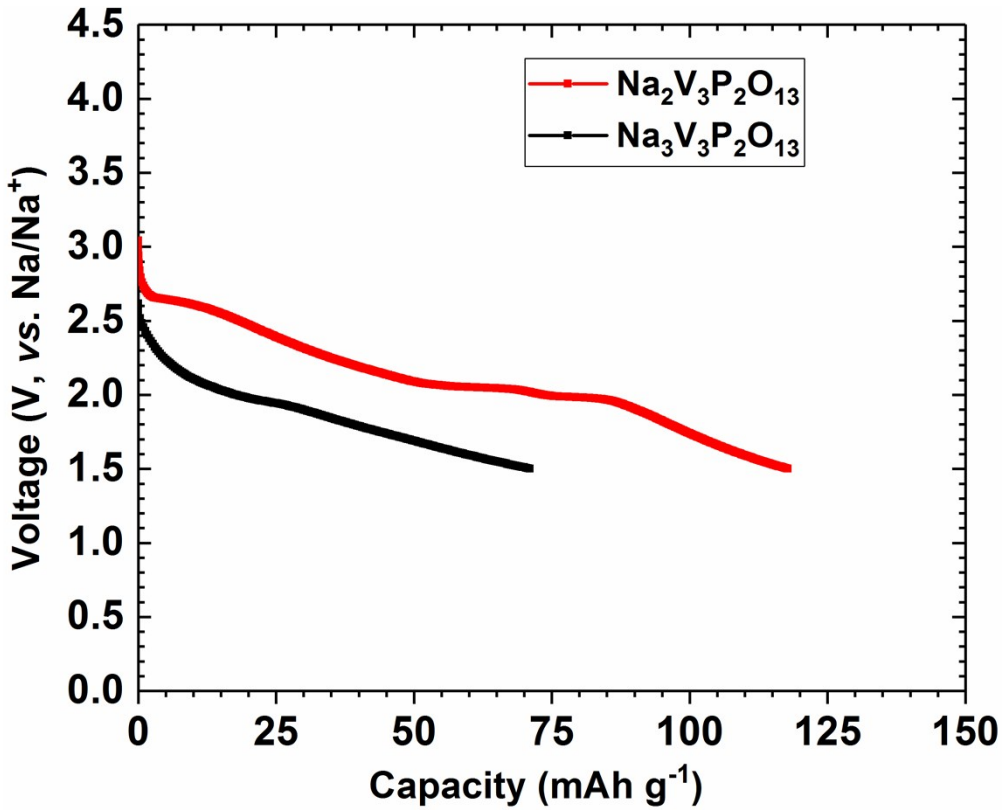

Figure S3 first discharge curves of $Na_2V_3P_2O_{13}$ and $Na_3V_3P_2O_{13}$. The discharge curves were obtained at 25 °C, at a current rate of C/20 and the cells were discharged to 1.5 V *vs*. Na/Na^+. Capacities were calculated based on the weight of the active material.

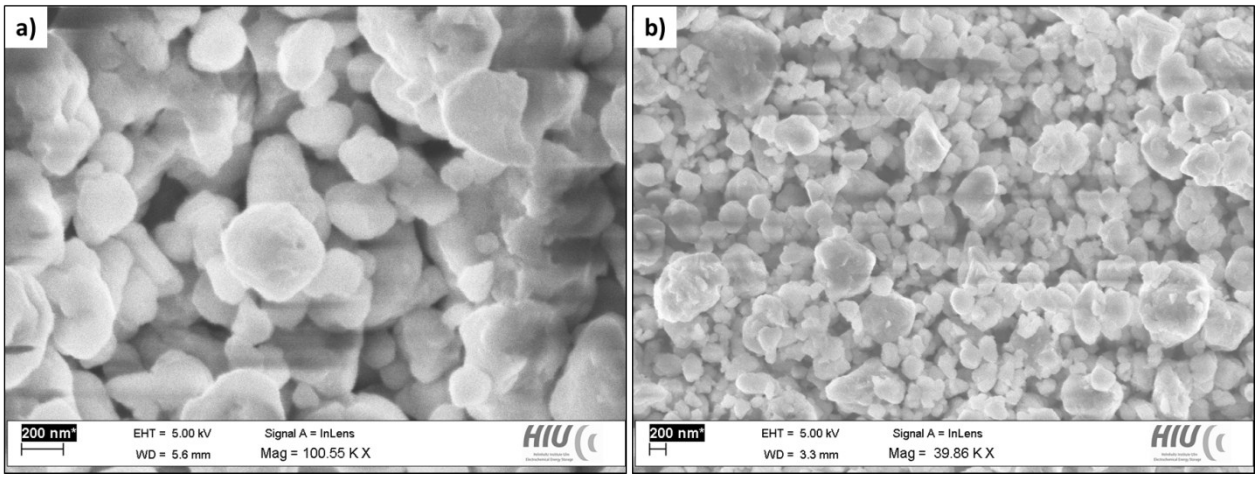

Figure S4 SEM images of a) $Na_2V_3P_2O_{13}$ and b) $Na_3V_3P_2O_{13}$

Table S2. Structural data of $Na_2V_3P_2O_{13}$ determined from Rietveld analysis of X-ray powder diffraction data. Oxidation states of the different vanadium ions are assigned according to determination of bond distances in agreement with DFT based calculations reported in section 0.

Wyckoff site / site label	atom type	x	y	z	occ.	B [Å²]
8e / Na1	Na^+	0.2155(4)	0.0464(3)	0.1075(4)	*1*	0.50(3)
8e / V1	V^{5+}	0.4796(2)	0.3676(2)	0.7555(3)	*1*	0.50(3)
4d / V2	V^{4+}	*1/4*	*3/4*	0.5624(4)	*1*	0.50(3)
8e / P1	P^{5+}	0.4849(3)	0.1249(5)	0.8715(3)	*1*	0.50(3)
8e / O1	O^{2-}	0.4288(6)	0.5037(5)	0.3046(8)	*1*	0.50(3)
8e / O2	O^{2-}	0.4216(5)	0.1450(4)	0.0469(7)	*1*	0.50(3)
8e / O3	O^{2-}	0.3513(5)	0.0862(5)	0.3544(7)	*1*	0.50(3)
8e / O4	O^{2-}	0.8682(5)	0.1160(5)	0.3921(6)	*1*	0.50(3)
8e / O5	O^{2-}	0.5903(5)	0.1489(5)	0.3940(7)	*1*	0.50(3)
8e / O6	O^{2-}	0.0635(5)	0.2093(5)	0.2437(7)	*1*	0.50(3)
4d / O7	O^{2-}	*1/4*	*3/4*	0.8672(10)	*1*	0.50(3)

a [Å]	10.1096(1)	**b [Å]**	11.9790(1)	**c [Å]**	8.3842(1)
R_{wp}	8.3 %	**R_{Bragg}**	3.3 %	**GOF**	1.12

Table S3. Structural data of chemically sodiated $Na_3V_3P_2O_{13}$ determined from Rietveld analysis of X-ray powder diffraction data. Oxidation states of the different vanadium ions are assigned according to determination of bond distances in agreement with DFT based calculations reported in section 0.

Wyckoff site / site label	atom type	x	y	z	occ.	B [Å²]
8e / Na1	Na^{+}	0.2245(4)	0.0050(4)	0.0723(7)	*1*	1.00(5)
4c / Na2	Na^{+}	*1/4*	*1/4*	0.5243(8)	*1*	1.00(5)
8e / V1	V^{4+}	0.4786(2)	0.3705(2)	0.7507(4)	*1*	1.00(5)
4d / V2	V^{5+}	*1/4*	*3/4*	0.6491(5)	*1*	1.00(5)
8e / P1	P^{5+}	0.4806(3)	0.1205(3)	0.8514(4)	*1*	1.00(5)
8e / O1	O^{2-}	0.4404(5)	0.4956(6)	0.2662(11)	*1*	1.00(5)
8e / O2	O^{2-}	0.4182(5)	0.1302(5)	0.0403(9)	*1*	1.00(5)
8e / O3	O^{2-}	0.3557(6)	0.1049(6)	0.3580(10)	*1*	1.00(5)
8e / O4	O^{2-}	0.8759(6)	0.1210(6)	0.3659(9)	*1*	1.00(5)
8e / O5	O^{2-}	0.6199(6)	0.1653(5)	0.3705(10)	*1*	1.00(5)
8e / O6	O^{2-}	0.0621(6)	0.2029(5)	0.2320(10)	*1*	1.00(5)
4d / O7	O^{2-}	*1/4*	*3/4*	0.8436(16)	*1*	1.00(5)
a [Å]	10.3095(4)	**b [Å]**	12.5169(4)	**c [Å]**	8.0943(3)	
R_{wp}	3.2 %	**R_{Bragg}**	0.9 %	**GOF**	1.33	

Table S4. Structural data of chemically prepared $Na_{2-x}V_3P_2O_{13}$ determined from Rietveld analysis of X-ray powder diffraction data. Refinement of the Na site occupation did not prove to be stable and was therefore fixed to a value determined independently.

Wyckoff site / site label	atom type	x	y	z	occ.	B [Å²]
8e / Na1	Na^{+}	0.2145(3)	0.0466(2)	0.1040(3)	*0.908(4)*	1.19(3)
8e / V1	V^{5+}	0.4801(1)	0.3669(1)	0.7556(2)	*1*	1.19(3)
4d / V2	V^{5+}	*1/4*	*3/4*	0.5616(2)	*1*	1.19(3)
8e / P1	P^{5+}	0.4878(2)	0.1203(2)	0.8720(2)	*1*	1.19(3)
8e / O1	O^{2-}	0.4363(3)	0.5009(3)	0.2980(5)	*1*	1.19(3)
8e / O2	O^{2-}	0.4215(3)	0.1417(3)	0.0453(5)	*1*	1.19(3)
8e / O3	O^{2-}	0.3513(4)	0.0870(3)	0.3481(5)	*1*	1.19(3)
8e / O4	O^{2-}	0.8671(3)	0.1216(3)	0.3886(4)	*1*	1.19(3)
8e / O5	O^{2-}	0.5919(3)	0.1499(3)	0.3802(4)	*1*	1.19(3)
8e / O6	O^{2-}	0.0593(3)	0.2049(3)	0.2456(5)	*1*	1.19(3)
4d / O7	O^{2-}	*1/4*	*3/4*	0.8807(6)	*1*	0.50(3)
a [Å]	10.1882(2)	**b [Å]**	11.9785(3)	**c [Å]**	8.3832(2)	
R_{wp}	3.5 %	**R_{Bragg}**	1.7 %	**GOF**	1.50	

Table S5. Refined bond distances of $Na_2V_3P_2O_{13}$ together with most likely assignment of vanadium oxidation states in agreement with DFT based calculations and bond distances which would be expected from Shannon's ionic radii.

d(Na1-Ox) [Å]		**d(V1-Ox) [Å] (8*e* site)**		**d(V2-Ox) [Å] (4*d* site)**		**d(P1-Ox) [Å]**	
O3	2.274(7)	O5	1.625(6)	O7	1.637(9)	O4	1.499(6)
O1	2.288(7)	O3	1.636(6)	O4	2.037(6)	O7	1.552(7)
O2	2.448(7)	O2	1.851(6)	O4	2.037(6)	O2	1.622(7)
O4	2.484(7)	O1	1.868(6)	O5	2.051(5)	O1	1.735(7)
O3	2.533(7)	O6	1.948(7)	O5	2.051(5)		
O5	2.660(7)			O7	2.555(9)		
O6	2.736(7)						
O1	3.382(8)						
d_{mean}	2.60	d_{mean}	1.79	d_{mean}	1.96 (CN=5) 2.06 (CN=6)	d_{mean}	1.60

Table S6. Refined bond distances of chemically sodiated $Na_3V_3P_2O_{13}$ together with most likely assignment of vanadium oxidation states in agreement with DFT based calculations and bond distances which would be expected from Shannon's ionic radii [13].

d(Na1-Ox) [Å]		**d(Na2-Ox) [Å]**		**d(V1-Ox) [Å] (8*e* site)**		**d(V2-Ox) [Å] (4*d* site)**		**d(P1-Ox) [Å]**	
O4	2.274(8)	O2	2.296(6)	O3	1.567(7)	O7	1.574(14)	O6	1.481(8)
O3	2.293(9)	O2	2.296(6)	O5	1.806(7)	O5	1.717(6)	O4	1.484(7)
O1	2.314(9)	O3	2.510(8)	O2	1.813(8)	O5	1.717(6)	O1	1.661(8)
O5	2.433(7)	O3	2.510(8)	O1	1.878(8)	O4	2.075(7)	O2	1.663(8)
O2	2.551(7)	O6	2.631(9)	O6	2.145(7)	O4	2.075(7)		
O3	2.957(9)	O6	2.631(9)			O7	2.473(14)		
O6	3.257(8)	O6	3.114(9)						
O1	3.331(9)	O6	3.114(9)						
		O3	3.433(9)						
		O3	3.433(9)						
d_{mean}	2.68	d_{mean}	2.64	d_{mean}	1.84	d_{mean}	1.83 (CN=5) 1.94 (CN=6)	d_{mean}	1.57

Table S7. Lattice parameters obtained from DFT calculations on $Na_yV_3P_2O_{13}$ (y = 1-3).

compound	symmetry	a [Å]	b [Å]	c [Å]
$Na_1V_3P_2O_{13}$	*Pc*2$_1$*n*	10.250	12.103	8.439
$Na_2V_3P_2O_{13}$	*Pccn*	10.345	12.155	8.420
$Na_3V_3P_2O_{13}$	*Pccn*	10.4584	12.6304	8.111

Table S8. Calculated bond distances for DFT calculated structure optimizations of $Na_yV_3P_2O_{13}$ (y = 1-3).* := For $Na_1V_3P_2O_{13}$ bond distances as obtained for the ordering of sodium ions belonging to a lowering of symmetry are given exemplarily (*Pccn* → *Pc*2$_1$*n*), resulting in a splitting of the 8e site to two sites with 4-fold multiplicity.

d(V1-O) [Å] (8*e* site)				**d(V2-O) [Å] (4*d* site)**		
$Na_1V_3P_2O_{13}$* (V^{5+})		**$Na_2V_3P_2O_{13}$ (V^{5+})**	**$Na_3V_3P_2O_{13}$ (V^{4+})**	**$Na_1V_3P_2O_{13}$* (V^{5+})**	**$Na_2V_3P_2O_{13}$ (V^{4+})**	**$Na_3V_3P_2O_{13}$ (V^{5+})**
1.635 1.748 1.910 1.942 1.944	1.602 1.810 1.884 1.931 1.990	1.628 1.764 1.940 1.960 1.985	1.649 1.753 1.956 2.012 2.081	1.626 1.837 1.864 1.902 1.968 2.595	1.622 1.868 1.868 1.999 1.999 2.588	1.634 1.877 1.877 2.039 2.039 2.422
d_{mean}						
1.84	1.84	1.855	1.89	1.84 (CN=5) 1.97 (CN=6)	1.87 (CN=5) 1.99 (CN=6)	1.89 (CN=5) 1.98 (CN=6)

Table S9. Calculated voltages for sodium insertion and extraction steps of $Na_2V_3P_2O_{13}$. * := different distributions of sodium ions on the *8e* site were investigated, resulting in slightly different energies.

Reaction of respective cycling step	Theoretical voltage against metallic sodium [V]
$Na_3V_3P_2O_{13} \rightarrow Na_2V_3P_2O_{13} + Na^+ + e^-$	1.97
$Na_2V_3P_2O_{13} \rightarrow Na_1V_3P_2O_{13} + Na^+ + e^-$	3.23 - 3.29*