Supporting information

Recognition of $V^{3+}/V^{4+}/V^{5+}$ multielectron reactions in $Na_3V(PO_4)_2$: a potential high energy density cathode for sodium-ion batteries

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Table S1. V and Mn based polyanionic cathodes with multielectron reactions.

cathodes	redox couple	method	theoretical capacity (mAh/g)	theoretical energy density (Wh/kg)	Ref.
$Na_3MnTi(PO_4)_3$	$Mn^{2+}/Mn^{3+}/ Mn^{4+}$	XPS	117	450	[1]
$Na_3MnZr(PO_4)_3$	$Mn^{2+}/Mn^{3+}/Mn^{4+}$	XPS	107	401	[2]
$Na_3VCr(PO_4)_3$	$V^{3+}/V^{4+}/V^{5+}$	XANES, ^{51}V NMR	117	439	[3]
$Na_3VAl(PO_4)_3$	$V^{3+}/V^{4+}/V^{5+}$	-	124	465	[4]
$Na_4VFe(PO_4)_3$	Fe^{2+}/Fe^{3+}, $V^{3+}/V^{4+}/V^{5+}$	Mössbauer spectra	166	548	[5]
$Na_4MnV(PO_4)_3$	$Mn^{2+}/Mn^{3+}/Mn^{4+}$, $V^{3+}/V^{4+}/V^{5+}$	-	167	601	[6-7]
$Na_3V_2(PO_4)_2F_3$	$V^{3+}/V^{4+}/V^{5+}$	sXAS, XANES	192	810	[8-9]
$Na_3V(PO_4)_2$	$V^{3+}/V^{4+}/V^{5+}$	^{51}V NMR	173	657	this work

Table S2. Atomic parameters for $Na_3V(PO_4)_2$.

Atom	Wyckoff site	*x*	*y*	*z*	Occupancy	100*U_{iso}
V	4*a*	0	0	0	1	2.33(7)
Na1	4*e*	0	0.0445(11)	0.25	1*	4.73(17)
Na2	8*f*	0.1704(4)	0.5375(7)	0.13424(17)	1*	2.52(10)
P	8*f*	0.16835(28)	0.5218(5)	0.38712(12)	1	2.12(6)
O1	8*f*	0.1658(5)	0.3890(8)	0.28908(25)	1	3.44(12)
O2	8*f*	0.1114(4)	0.3264(8)	0.45872(23)	1	2.50(11)
O3	8*f*	0.0811(4)	0.7863(7)	0.38498(26)	1	2.46(10)
O4	8*f*	0.3306(4)	0.5925(7)	0.41351(26)	1	2.13(10)

* The occupancy of Na is slightly larger than 1, which may be caused by calculating error. Consequently, the value is fixed to 1 during the refinement.

Table S3. Selected bond distance (Å) for $Na_3V(PO_4)_2$.

V-O2	2.020(4)	Na2-O1	2.274(5)
V-O3	2.072(4)	Na2-O1’	2.532(6)
V-O4	1.986(4)	Na2-O2	2.573(5)
P-O1	1.514(5)	Na2-O2’	2.797(5)
P-O2	1.498(5)	Na2-O3	2.608(6)
P-O3	1.550(5)	Na2-O3’	2.616(6)
P-O4	1.553(5)	Na2-O4	2.336(5)
Na1-O1	2.353(6)	Na2-O4’	2.872(5)
Na1-O3	2.382(5)		
Na1-O4	2.778(4)		

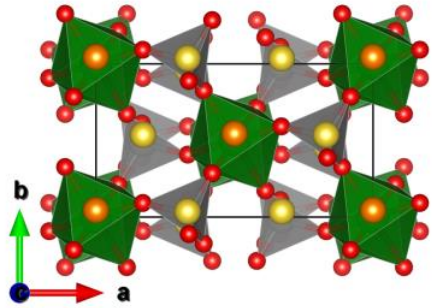

Figure S1. Crystal structure of $Na_3V(PO_4)_2$.

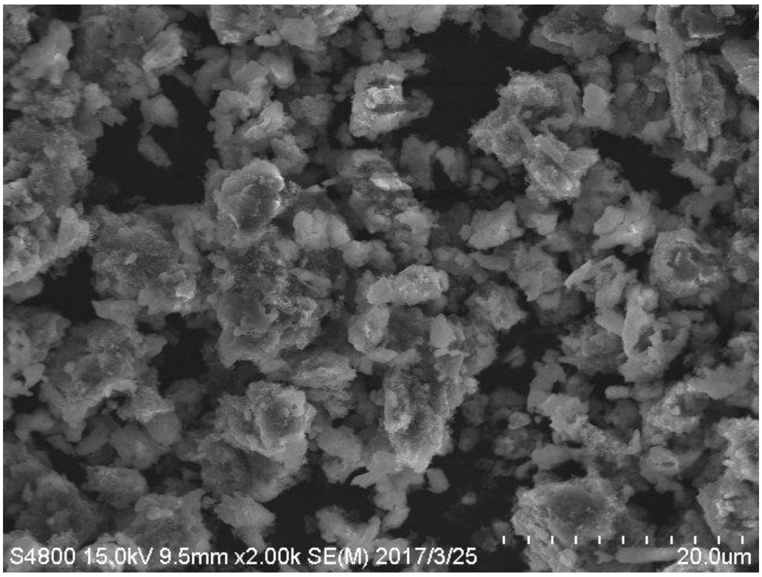

Figure S2. SEM image of $Na_3V(PO_4)_2$.

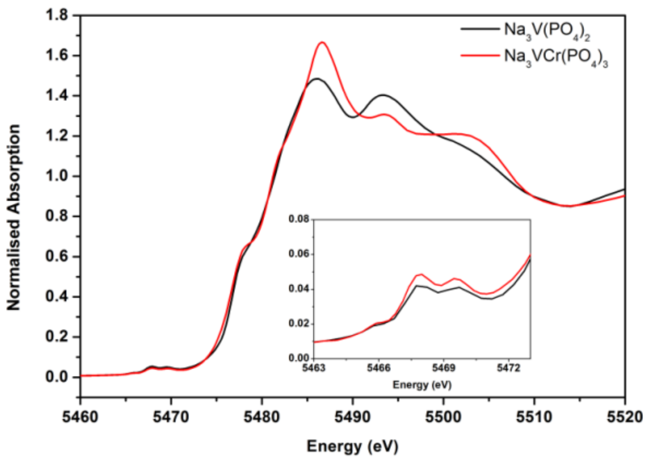

Figure S3. XANES spectra of of $Na_3V(PO_4)_2$ and $Na_3VCr(PO_4)_3$.

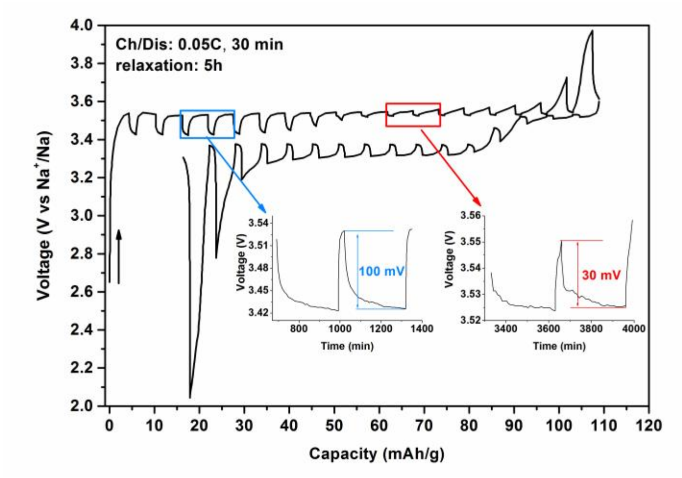

Figure S4. QOCV curve of $Na_3V(PO_4)_2$ cathode in the voltage range of 2.5 – 3.8 V.

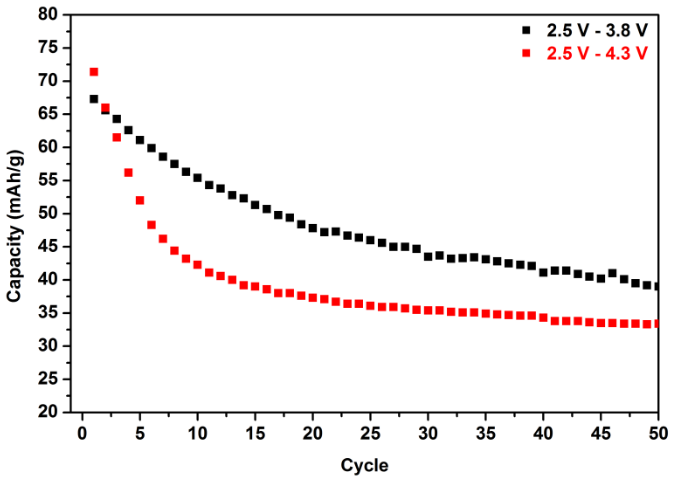

Figure S5. Cycling performance of $Na_3V(PO_4)_2$ cathode.

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