Supporting Information for

$NaV_{1.25}Ti_{0.75}O_4$: a potential post spinel cathode material for Mg batteries

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List of Supporting Tables

Table S1a. Refined parameters for the pristine $NaV_{1.25}Ti_{0.75}O_4$ with 1:0.19 standard Si (χ^2 = 4.20). The V/Ti mixing cannot be refined from XRD data so the occupancies were fixed at values reported in the initial reference from neutron diffraction.[1] The exact formula is $NaV_{1.23}Ti_{0.77}O_4$, but the original paper used a simplied notation of $NaV_{1.25}Ti_{0.75}O_4$ and we have kept this in order to be consistent.

Atom	Wyck.	*x*	*y*	*z*	Occ.	B_{iso} (Å^2)
$NaV_{1.25}Ti_{0.75}O_4$, space group = *Pmnb*, *a* = 2.9466(2) Å, *b* = 9.1667(3) Å, *c* = 10.6703(4) Å, 83(2) wt%, Bragg *R*-factor = 3.37						
Na	4c	0.75	0.2436(7)	0.3479(6)	1	1.2(2)
Ti1	4c	0.75	0.0658(3)	0.1110(3)	0.45	0.61(7)
V1	4c	0.75	0.0658(3)	0.1110(3)	0.55	0.61(7)
Ti2	4c	0.75	0.0810(3)	0.6040(3)	0.32	0.53(7)
V2	4c	0.75	0.0810(3)	0.6040(3)	0.68	0.53(7)
O1	4c	0.75	0.2924(9)	0.6508(8)	1	0.73(7)
O2	4c	0.75	0.3884(8)	0.9795(9)	1	0.73(7)
O3	4c	0.75	0.4773(3)	0.2169(3)	1	0.73(7)
O4	4c	0.75	0.0772(3)	0.9263(3)	1	0.73(7)
Si, space group = *Fd*-3*m*, *a* = 5.43185(9) Å, 17.0(4) wt%, Bragg *R*-factor = 3.44						
Si	8a	0.875	0.875	0.875	1	0.70(3)

Table S1b. Refined parameters for the chem-ox-1 sample with 1:0.51 standard Si (χ^2 = 5.68).

Atom	Wyck.	*x*	*y*	*z*	Occ.	B_{iso} (Å^2)
$Na_{0.36}V_{1.25}Ti_{0.75}O_4$, space group = *Pmnb*, *a* = 2.9365(2) Å, *b* = 8.9540(9) Å, *c* = 10.6493(4) Å, 66(2) wt%, Bragg *R*-factor = 3.38						
Na	4c	0.75	0.233(3)	0.342(2)	0.358(9)	1.2
Ti1	4c	0.75	0.0560(4)	0.1155(3)	0.45	0.89(8)
V1	4c	0.75	0.0560(4)	0.1155(3)	0.55	0.89(8)
Ti2	4c	0.75	0.0829(5)	0.6013(3)	0.32	1.38(8)
V2	4c	0.75	0.0829(5)	0.6013(3)	0.68	1.38(8)
O1	4c	0.75	0.304(2)	0.6463(9)	1	1.32(9)
O2	4c	0.75	0.397(1)	0.9829(9)	1	1.32(9)
O3	4c	0.75	0.480(2)	0.2134(8)	1	1.32(9)
O4	4c	0.75	0.074(2)	0.9279(6)	1	1.32(9)
Si, space group = *Fd*-3*m*, *a* = 5.43155(6) Å, 33.9(5) wt%, Bragg *R*-factor = 2.90						
Si	8a	0.875	0.875	0.875	1	0.67(2)

Table S1c. Refined parameters for the chem-ox-2 sample with 1:0.20 standard Si (χ^2 = 3.81).

Atom	Wyck.	*x*	*y*	*z*	Occ.	B_{iso} (Å^2)
$Na_{0.25}V_{1.25}Ti_{0.75}O_4$, space group = *Pmnb*, *a* = 2.9392(2) Å, *b* = 8.8827(6) Å, *c* = 10.6434(4) Å, 76(2) wt%, Bragg *R*-factor = 2.64						
Na	4c	0.75	0.235(3)	0.337(2)	0.248(8)	1.2
Ti1	4c	0.75	0.0539(3)	0.1171(3)	0.45	0.80(7)
V1	4c	0.75	0.0539(3)	0.1171(3)	0.55	0.80(7)
Ti2	4c	0.75	0.0855(4)	0.6018(3)	0.32	1.37(7)
V2	4c	0.75	0.0855(4)	0.6018(3)	0.68	1.37(7)
O1	4c	0.75	0.3037(9)	0.6463(7)	1	1.05(8)
O2	4c	0.75	0.3917(9)	0.9865(7)	1	1.05(8)
O3	4c	0.75	0.476(1)	0.2148(7)	1	1.05(8)
O4	4c	0.75	0.076(1)	0.9284(5)	1	1.05(8)
Si, space group = *Fd*-3*m*, *a* = 5.43189(6) Å, 23.6(4) wt%, Bragg *R*-factor = 2.88						
Si	8a	0.875	0.875	0.875	1	0.69(2)

Table S1d. Refined parameters for the Mg-ex sample with 1:0.20 standard Si (χ^2 = 5.03).

Atom	Wyck.	*x*	*y*	*z*	Occ.	B_{iso} (Å^2)
$Na_{0.19}Mg_{0.41}V_{1.25}Ti_{0.75}O_4$, space group = *Pmnb*, *a* = 2.9320(2) Å, *b* = 9.0701(4) Å, *c* = 10.6609(5) Å, 82(2) wt%, Bragg *R*-factor = 4.63						
Na[†]	4c	0.75	0.243(2)	0.3452(9)	0.190(7)	1.2
Mg[†]	4c	0.75	0.243(2)	0.3452(9)	0.405(7)	1.2
Ti1	4c	0.75	0.0630(3)	0.1122(3)	0.45	0.63(8)
V1	4c	0.75	0.0630(3)	0.1122(3)	0.55	0.63(8)
Ti2	4c	0.75	0.0834(4)	0.6030(3)	0.32	1.14(8)
V2	4c	0.75	0.0834(4)	0.6030(3)	0.68	1.14(8)
O1	4c	0.75	0.2872(9)	0.6464(9)	1	1.5(1)
O2	4c	0.75	0.391(1)	0.9796(9)	1	1.5(1)
O3	4c	0.75	0.4802(4)	0.2142(3)	1	1.5(1)
O4	4c	0.75	0.0773(3)	0.9236(3)	1	1.5(1)
Si, space group = *Fd*-3*m*, *a* = 5.4317(2) Å, 17.8(4) wt%, Bragg *R*-factor = 2.92						
Si	8a	0.875	0.875	0.875	1	0.66(3)

[†] Since Mg and Na have almost identical atomic scattering factors, we initially refined that site occupancy to 0.59. Some fraction of this must be Mg^{2+} (since the total charge on the site should be 1.0). Based on that consideration, equation (n + 2m = 1) defines n as the Na fraction and m as the Mg fraction, and provides values of n = 0.19 and m = 0.41. These values were then refined, and converged to the values shown in the table.

Table S2. Crystalline phase weight percentages estimated by standard Si addition

Sample	Sample:Si weight ratio	CF:Si weight ratio from Rietvied	Crystalline wt%
Pristine	1:0.19	0.83(2):0.170(4)	93(5)%
Chem-ox-1	1:0.51	0.66(2):0.339(5)	99(5)%
Chem-ox-2	1:0.20	0.76(2):0.236(4)	64(4)%
Mg-ex	1:0.20	0.82(2):0.178(4)	92(5)%

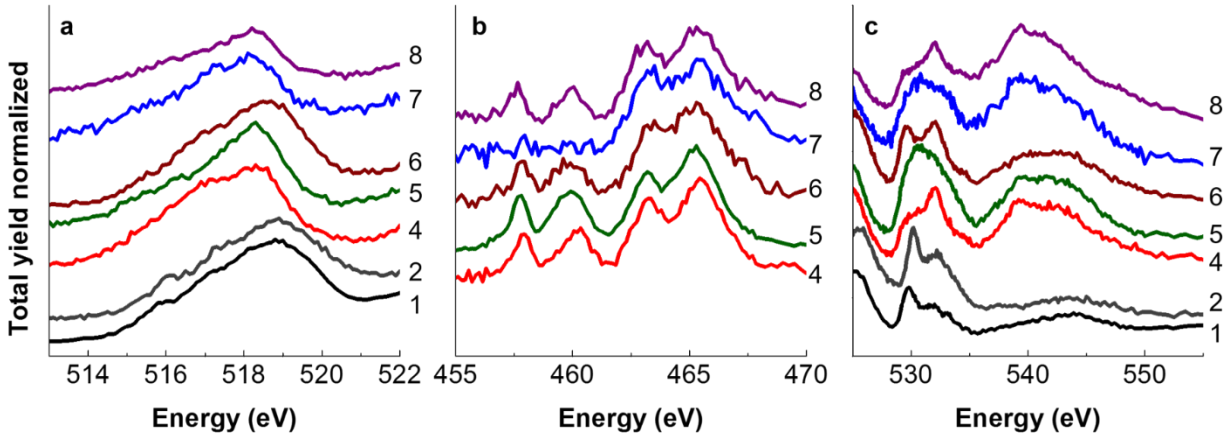

Figure S1. X-ray near edge absorption spectroscopy (XANES) normalized fluorescence yields for the materials examined in this study; (a) V L and O K edges between 513 – 522 eV; (b) Ti L edge between 455 – 470 eV; and (c) V L and O K edges between 525 – 550 eV. XANES data for standards correspond to: (1) VO_2; (2) V_2O_5; (4) pristine $NaV_{1.25}Ti_{0.75}O_4$. XANES data for $NaV_{1.25}Ti_{0.75}O_4$ subjected to various treatments are shown as follows: ((5) Chem-ox-1, (6) Chem-ox-2)), (7) electrochemically charged and (8) chemically magnesiated. Please see main text for details.

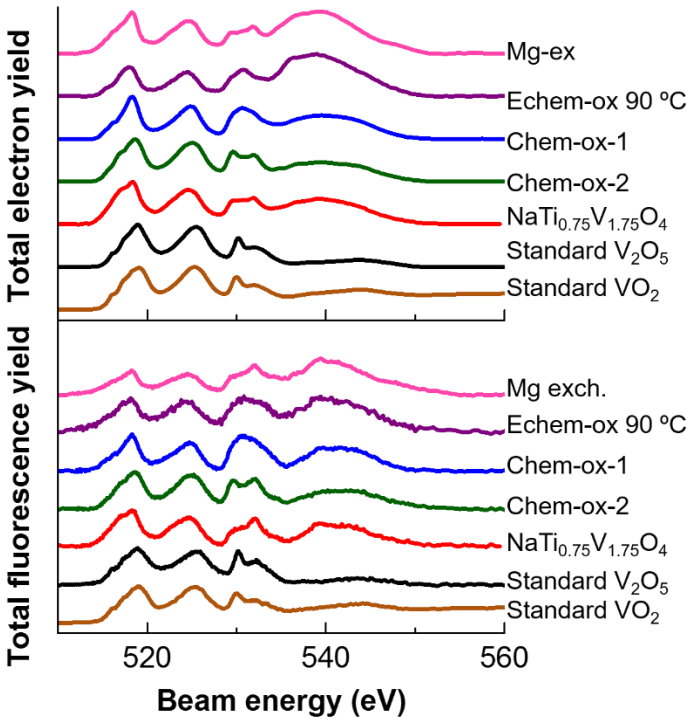

Figure S2. XANES spectra for materials as labelled; both electron (top) and fluorescence (bottom) yields corrresponding to the V L- and O K-edges are shown.

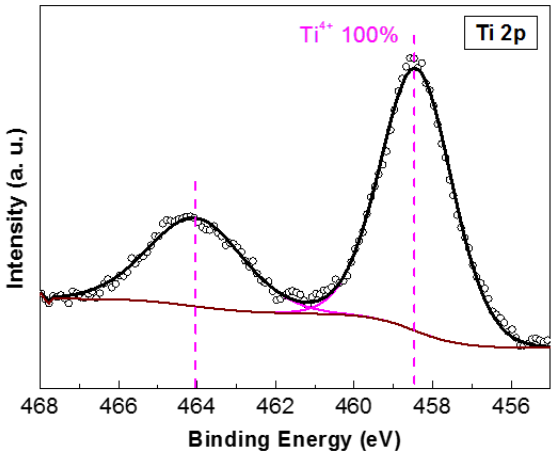

Figure S3. Ti 2p XPS spectrum of pristine $NaV_{1.25}Ti_{0.75}O_4$, showing a binding energy characteristic of Ti^{4+} at 458.4 eV ($2p_{3/2}$).

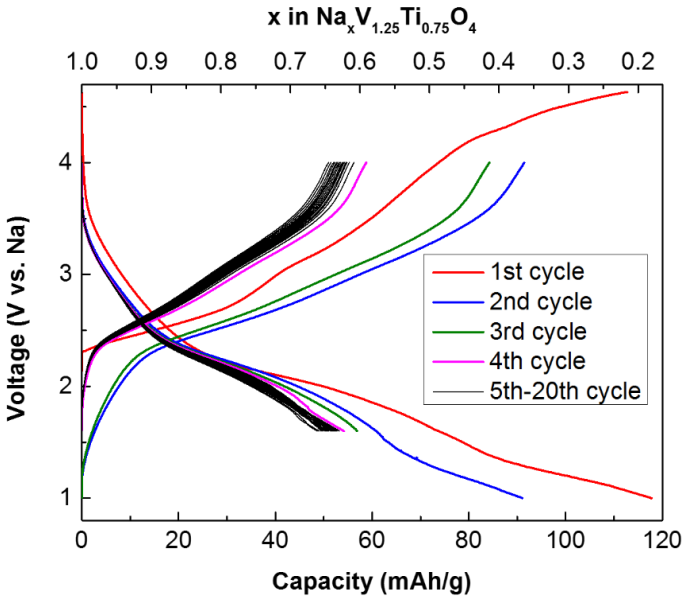

Figure S4. Electrochemistry of $NaV_{1.25}Ti_{0.75}O_4$ with a Na anode and an electrolyte comprised of 1M $NaClO_4$ in PC with 2 vol% FEC at 5 mA g^{-1} current density and room temperature. The voltage window was limited to 1.5 – 4 V after the 4th cycle, since we noted that partial electrolyte decomposition would contribute to capacity at voltage above 4 V, whereas discharging to low voltage might lead to the uptake of Na beyond the composition of $NaV_{1.25}Ti_{0.75}O_4$.

REFERENCES

[1] Viciu, L.; Ryser, A.; Mensing, C.; Bos, J.-W. G. Ambient-Pressure Synthesis of Two New Vanadium-Based Calcium Ferrite-Type Compounds: $NaV_{1.25}Ti_{0.75}O_4$ and $NaVSnO_4$. *Inorg. Chem.* **2015**, *54*, 7264-7271.