

Supporting Information

Structural and Electrochemical Insights into novel Nb₇Ti_{1.5}Mo_{1.5}O₂₅
and Ta₇Ti_{1.5}Mo_{1.5}O₂₅ anodes for High-Power Li-ion Battery Application

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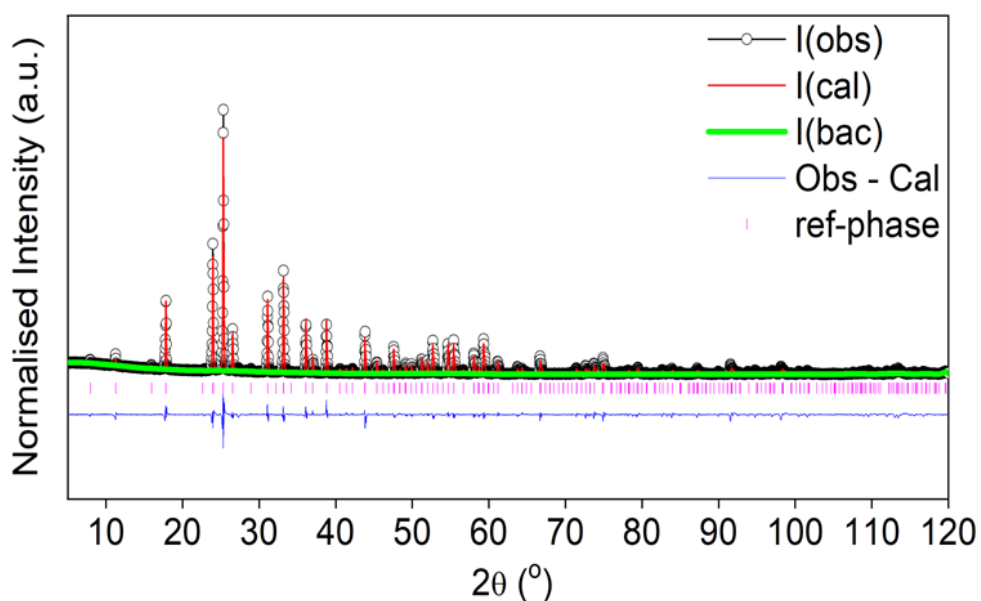
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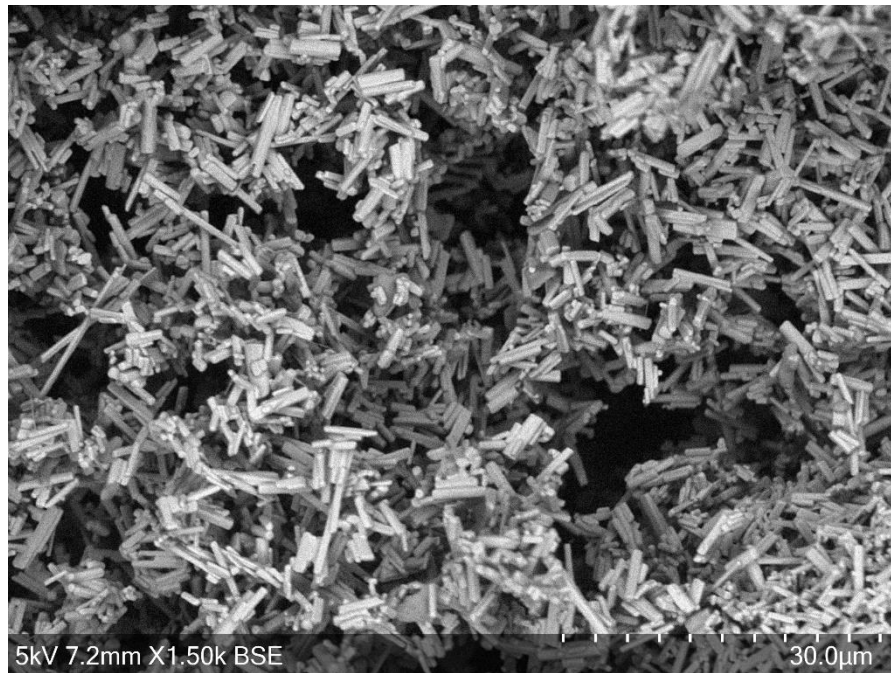
SI Figure 1: Observed, calculated and difference XRD profiles for TTMO71515 ($R_{wp} = 9.51\%$, $R_p = 6.25\%$) (Cu $K\alpha$) through a Rietveld refinement on GSAS II.

SI Table 1: Refined structural parameters for NTMO71515. Due to the presence of multiple cations, including isoelectronic Nb^{5+} and Mo^{6+} , and low X-ray scattering of the oxygen, the refinement was conducted in stages – with the starting point involving all octahedral cation sites set to Nb^{5+} , with Mo^{6+} in the tetrahedral site (due to the known greater preference of Mo^{6+} for tetrahedral coordination). Sites which showed low Nb content were then assumed to be occupied by Ti. Note to match the sample formula, some Mo must also be on the other Nb sites (site 2-4), but the value was not possible to refine due to the fact that Mo^{6+} and Nb^{5+} are isoelectronic and so possess the same X-ray scattering factor.

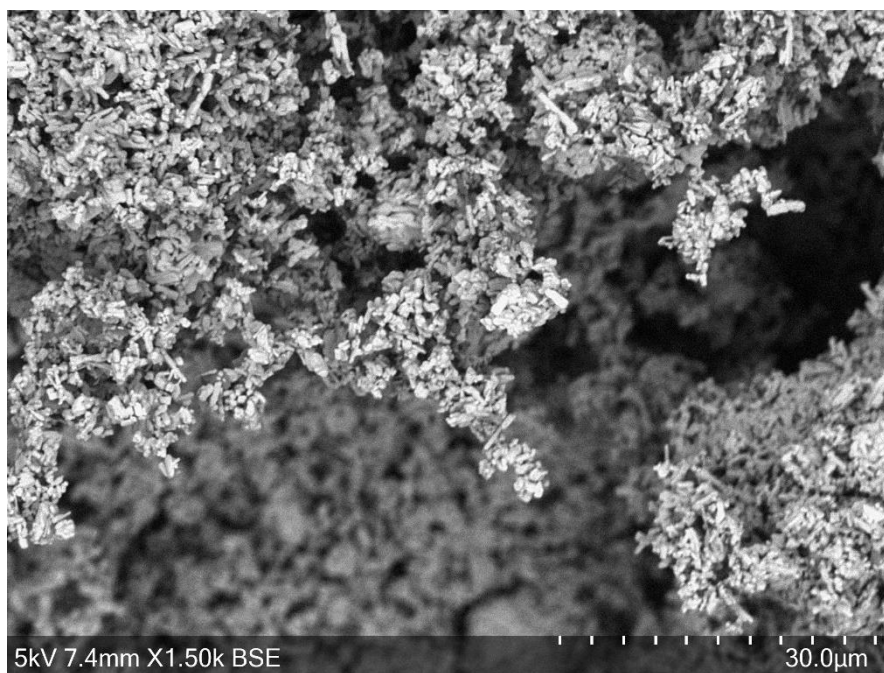
Cation Site	Label	Multiplicity	x	y	z	Fraction	U_{iso}
Site 1	Ti1	2	0.00000	0.50000	0.2500	0.078 (11)	0.02000
	Mo1	2	0.00000	0.50000	0.2500	0.922 (11)	0.02000
Site 2	Ti2	2	0.00000	0.00000	0.00000	0.088 (10)	0.02000
	Nb2	2	0.00000	0.00000	0.00000	0.912 (10)	0.02000
Site 3	Ti3	8	0.2209 (6)	0.1015 (5)	0.037 (3)	0.043 (4)	0.02000
	Nb3	8	0.2209 (6)	0.1015 (5)	0.037 (3)	0.957 (4)	0.02000
Site 4	Ti4	8	0.1331 (5)	0.3164 (5)	0.973 (3)	0.204 (9)	0.02000
	Nb4	8	0.1331 (5)	0.3164 (5)	0.973 (3)	0.796 (9)	0.02000
	O1	2	0.00000	0.00000	0.50000	1.000	0.02000
	O2	8	0.257 (2)	0.387 (4)	-0.01 (2)	1.000	0.02000
	O3	8	0.110 (3)	0.055 (3)	0.03 (2)	1.000	0.02000
	O4	8	0.222 (4)	0.114 (4)	0.69 (1)	1.000	0.02000
	O5	8	0.028 (2)	0.272 (2)	1.00 (2)	1.000	0.02000
	O6	8	0.061 (2)	0.457 (4)	0.94 (1)	1.000	0.02000
	O7	8	0.793 (2)	0.379 (3)	0.06 (2)	1.000	0.02000

SI Table 2: Refined structural parameters for TTMO71515. Note to match the sample formula, some Mo must also be on the other Ta sites (site 2-4) but given the presence of 3 elements on these sites (Ta/Mo/Ti) it was not possible to refine all three together. Therefore, the reported Ti/Ta occupancies should be treated as simply guidelines for the relative distribution over the sites.

Cation Site	Label	Multiplicity	x	y	z	Fraction	U _{iso}
Site 1	Mo1	2	0.00000	0.50000	0.2500	0.98 (2)	0.02000
	Ti1	2	0.00000	0.50000	0.2500	0.02 (2)	0.02000
Site 2	Ta2	2	0.00000	0.00000	0.0000	1.000	0.02000
Site 3	Ti3	8	0.2234 (6)	0.0944 (4)	0.009 (5)	0.27 (1)	0.02000
	Ta3	8	0.2234 (6)	0.0944 (4)	0.009 (5)	0.73 (1)	0.02000
Site 4	Ti4	8	0.1277 (5)	0.3180 (5)	0.99 (4)	0.20 (1)	0.02000
	Ta4	8	0.1277 (5)	0.3180 (5)	0.99 (4)	0.80 (1)	0.02000
	O1	2	0.00000	0.00000	0.50000	1.000	0.02000
	O2	8	0.300 (4)	0.367 (4)	0.44 (2)	1.000	0.02000
	O3	8	0.121 (3)	0.051 (4)	0.003 (23)	1.000	0.02000
	O4	8	0.258 (3)	0.128 (3)	0.51 (4)	1.000	0.02000
	O5	8	0.014 (3)	0.278 (4)	0.96 (3)	1.000	0.02000
	O6	8	0.075 (2)	0.447 (3)	0.03 (2)	1.000	0.02000
	O7	8	0.815 (3)	0.356 (3)	0.04 (2)	1.000	0.02000



SI Figure 2: Scanning electron microscopy (SEM) image of NTMO71515.



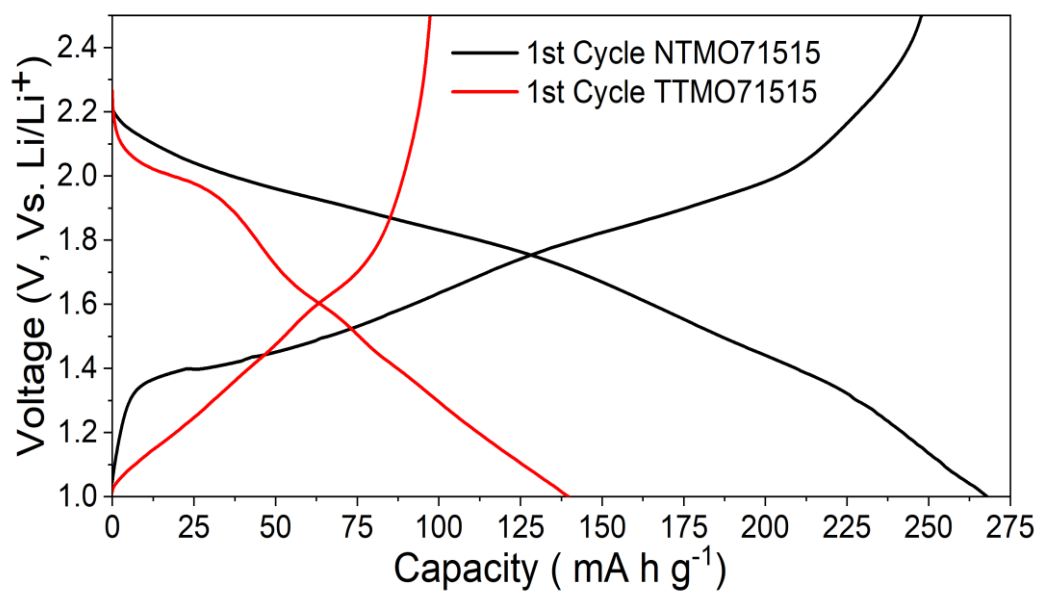
SI Figure 3: Scanning electron microscopy (SEM) image of TTMO71515.

SI Table 3: The corresponding capacity and calculated Li^+ intercalation for each voltage range for the 3 formation cycles of NTMO71515

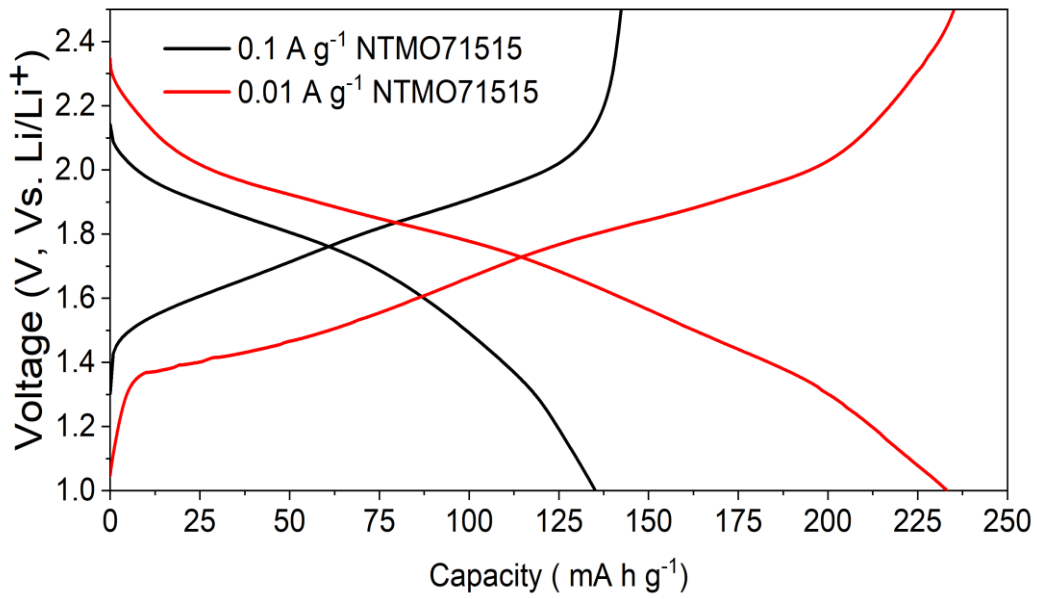
NTMO71515 1 st Cycle			NTMO71515 2 nd Cycle			NTMO71515 3 rd Cycle		
Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺	Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺	Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺
2.20 – 2.00	32	1.5	2.40 – 2.00	26	1.2	2.40 – 2.00	26	1.2
2.00 – 1.30	193	9.2	2.00 – 1.30	171	8	2.00 – 1.30	167	7.9
1.30 – 1.00	43	2	1.30 – 1.00	36	1.7	1.30 – 1.00	29	1.4
Total Li⁺		12.7	Total Li⁺		10.9	Total Li⁺		10.5

SI Table 4: The corresponding capacity and calculated amount of Li^+ intercalation for each voltage range for the 3 formation cycles of TTMO71515

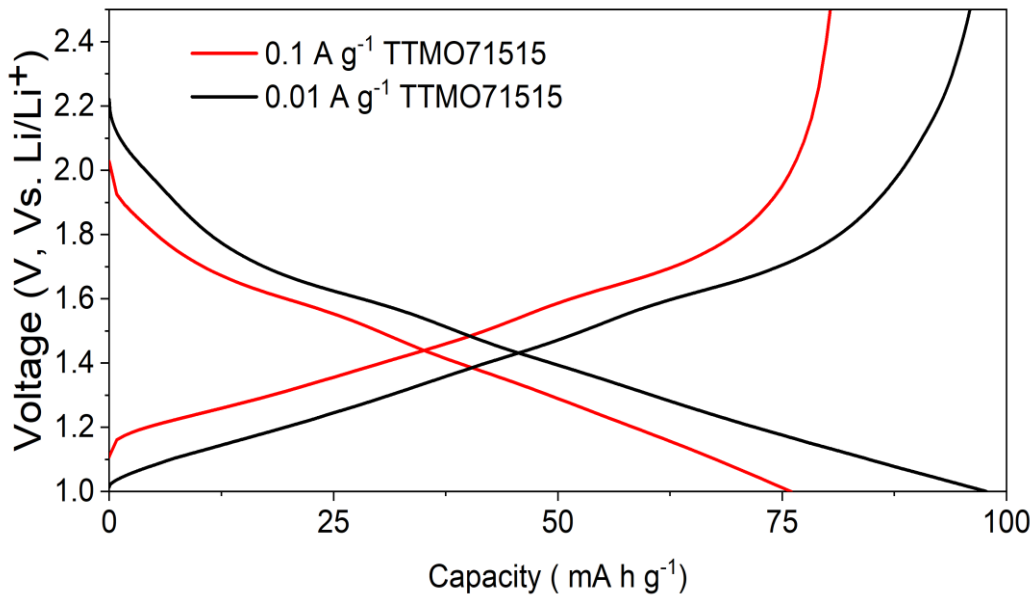
TTMO71515 1 st Cycle			TTMO71515 2 nd Cycle			TTMO71515 3 rd Cycle		
Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺	Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺	Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺
2.30 – 1.95	31	2.2	2.30 – 1.70	17	1.2	2.20 – 1.70	17	1.2
1.95 – 1.55	39	2.7	1.70 – 1.55	15	1.1	1.70 – 1.55	15	1.1
1.55 – 1.00	70	4.9	1.55 – 1.00	66	4.6	1.55 – 1.00	63	4.4
Total Li⁺		9.8	Total Li⁺		6.9	Total Li⁺		6.7



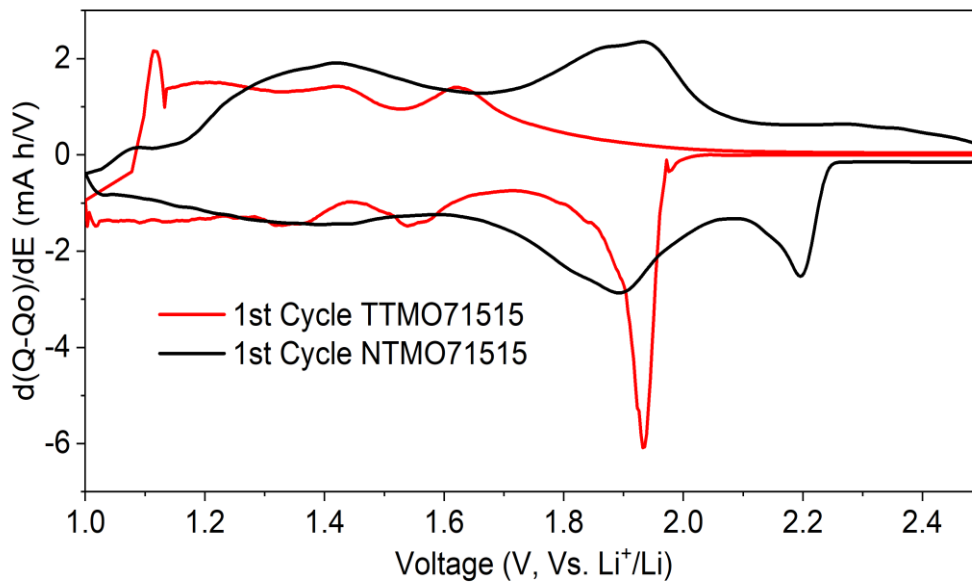
SI Figure 4: Galvanostatic discharge-charge curves for the 1st cycles of NTMO71515 and TTMO71515, with a current density of 0.01 A g⁻¹ applied.



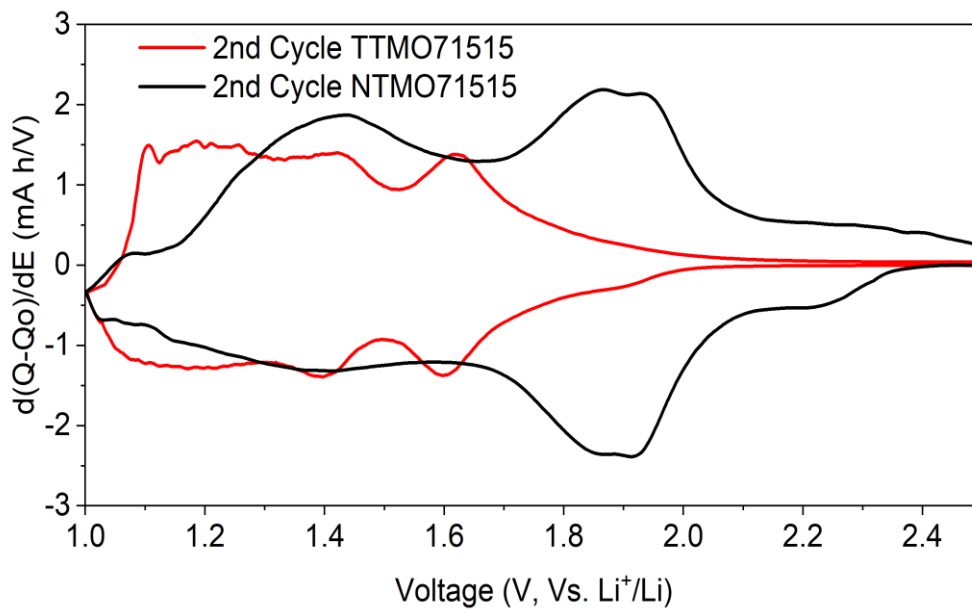
SI Figure 5: Galvanostatic discharge-charge curves for NTMO71515 at current densities of 0.01 and 0.1 A g⁻¹.



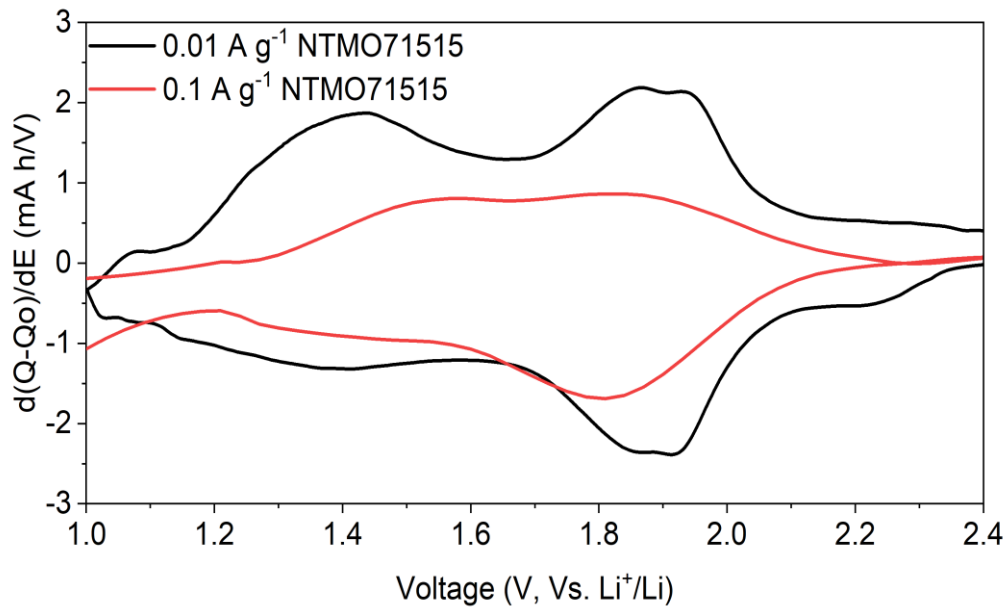
SI Figure 6: Galvanostatic discharge-charge curves for TTMO71515 at current densities of 0.01 and 0.1 A g⁻¹.



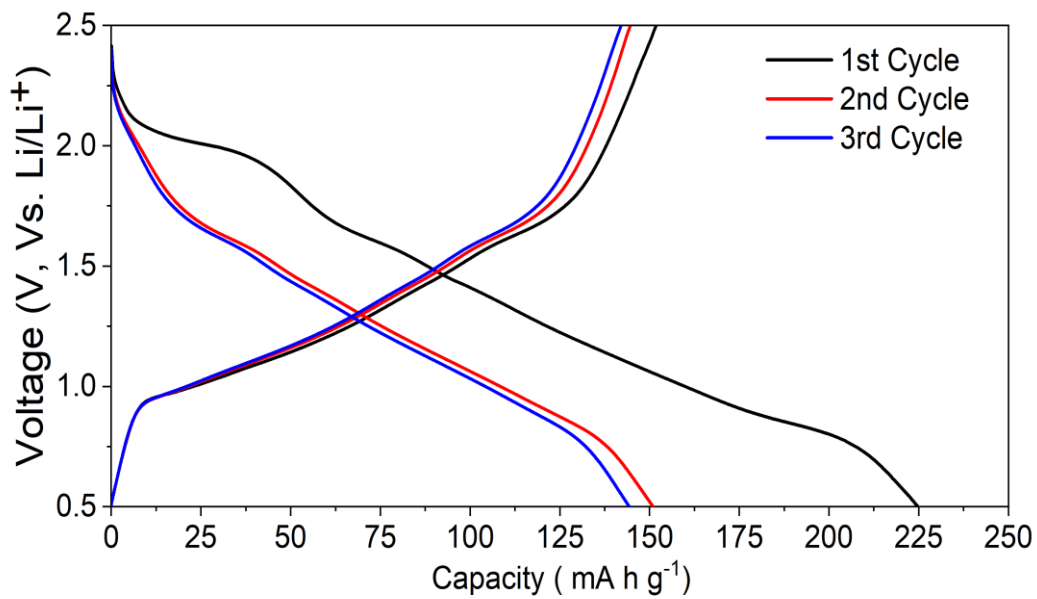
SI Figure 7: dQ/dV plots derived from the galvanostatic discharge-charge profiles of the 1st cycle comparing NTMO71515 and TTMO71515



SI Figure 8: dQ/dV plots derived from the galvanostatic discharge-charge profiles of the 2nd cycle comparing NTMO71515 and TTMO71515



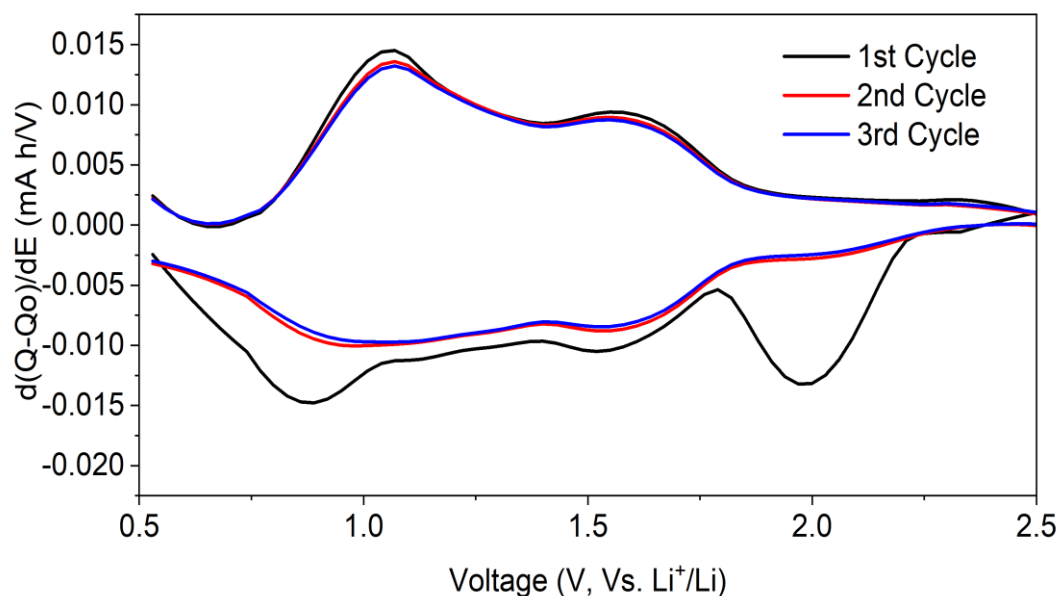
SI Figure 9: dQ/dV plots derived from the galvanostatic discharge-charge profiles of NTMO71515 at current densities of 0.01 and 0.1 A g⁻¹.



SI Figure 10: Galvanostatic discharge-charge curves for the 3 formation cycles at a current density of 0.01 A g⁻¹ between 0.5 -2.5 V for TMO71515

SI Table 5: The corresponding capacity and calculated Li^+ intercalation for each voltage range for the 1st and 2nd formation cycles of the 0.5 – 2.5 V voltage study for TTMO71515

TTMO71515 (2.5 – 0.5V) 1 st Cycle			TTMO71515 (2.5 – 0.5V) 2 nd Cycle		
Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺	Voltage Range (V)	Capacity (mA h g ⁻¹)	Amount of Li ⁺
2.40 – 2.00	32	2.2	2.40 – 1.60	36	2.5
2.00 – 0.85	158	11.1	1.60 – 0.80	97	6.8
0.85 – 0.50	35	2.5	0.80 – 0.50	18	1.3
Total Li⁺		15.5	Total Li⁺		10.6



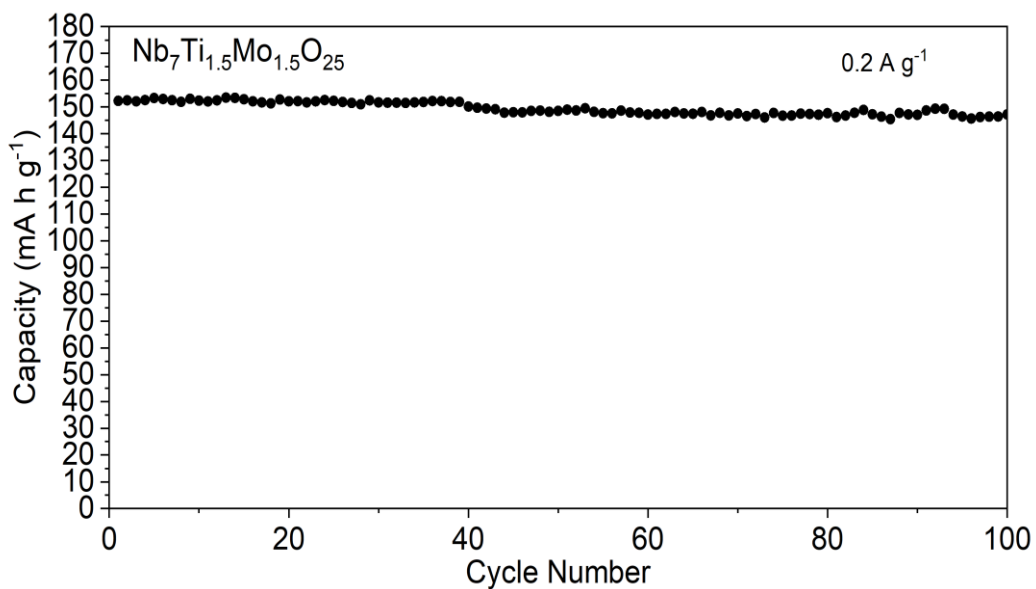
SI Figure 11: dQ/dV plots derived from the galvanostatic discharge-charge profiles for the 3 formation cycles at a current density of 0.01 A g^{-1} between 0.5 -2.5 V for TTMO71515

SI Table 6: The average capacity retention between the 1st and the final (5th) delithiation cycle at different current densities for NTMO71515. The corresponding C-rate for each for each current density is also shown.

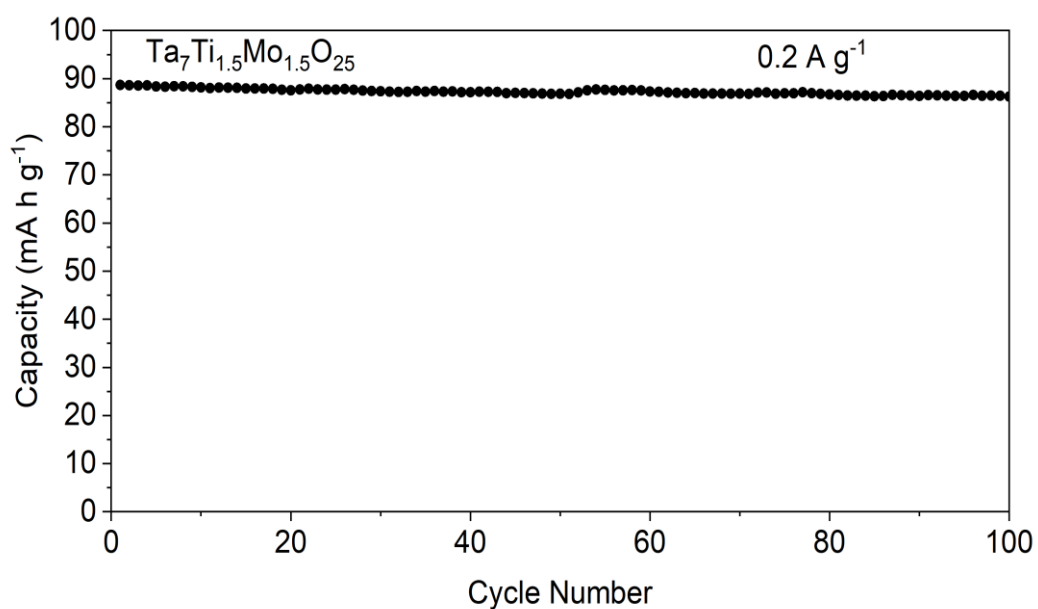
NTMO71515				
Current Density (A g⁻¹)	C-rate	1st Cycle (mA h g⁻¹)	Final Cycle (mA h g⁻¹)	Capacity Retention (%)
0.1	0.4	151 (12)	150 (12)	99
0.2	0.7	146 (13)	145 (11)	99
0.4	1.5	140 (11)	143 (13)	98
0.6	2.2	139 (13)	139 (10)	99
1	3.7	134 (10)	138 (13)	98
2	7.5	130 (13)	133 (10)	98
4	14.9	114 (14)	115 (21)	99
0.1	0.4	159 (14)	159 (11)	99

SI Table 7: The average capacity retention between the 1st and the final (5th) delithiation cycle at different current densities for TTMO71515. The corresponding C-rate for each for each current density is also shown.

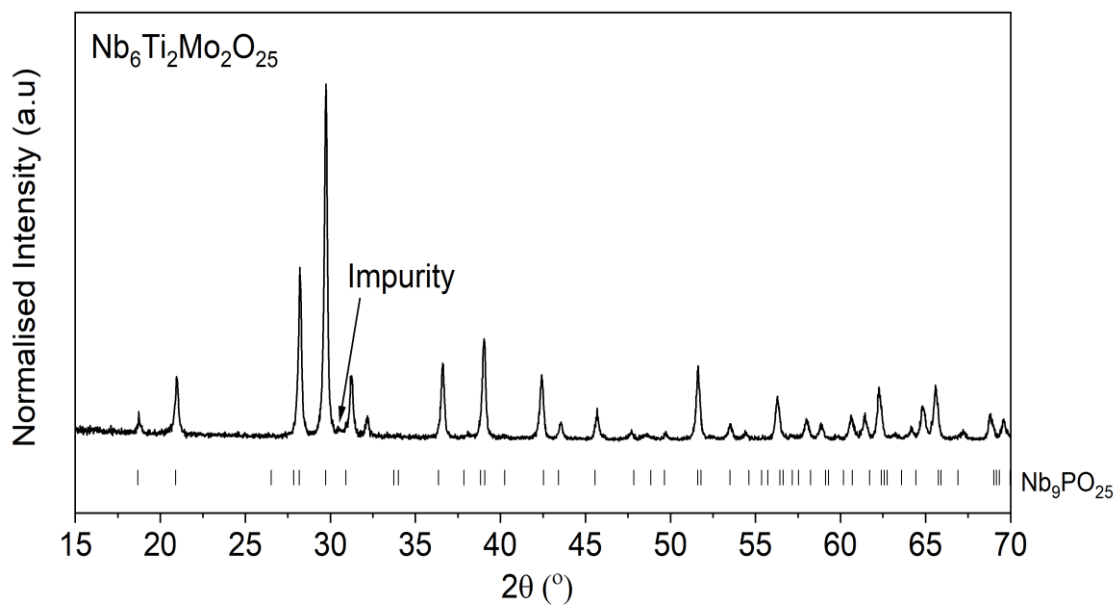
TTMO71515				
Current Density (A g⁻¹)	C-rate	1st Cycle (mA h g⁻¹)	Final Cycle (mA h g⁻¹)	Capacity Retention (%)
0.1	0.7	79 (2)	79 (3)	99
0.2	1.4	78 (1)	78 (1)	99
0.4	2.9	75 (2)	75 (2)	99
0.6	4.3	74 (2)	75 (3)	99
1	7.1	72 (2)	72 (2)	99
2	14.3	68 (1)	68 (1)	99
4	28.6	59 (1)	60 (2)	99
0.1	0.7	80 (2)	80 (3)	99



SI Figure 12: Long term cycling data for NTMO71515. 100 cycles were performed at a current density of 0.2 A g⁻¹.



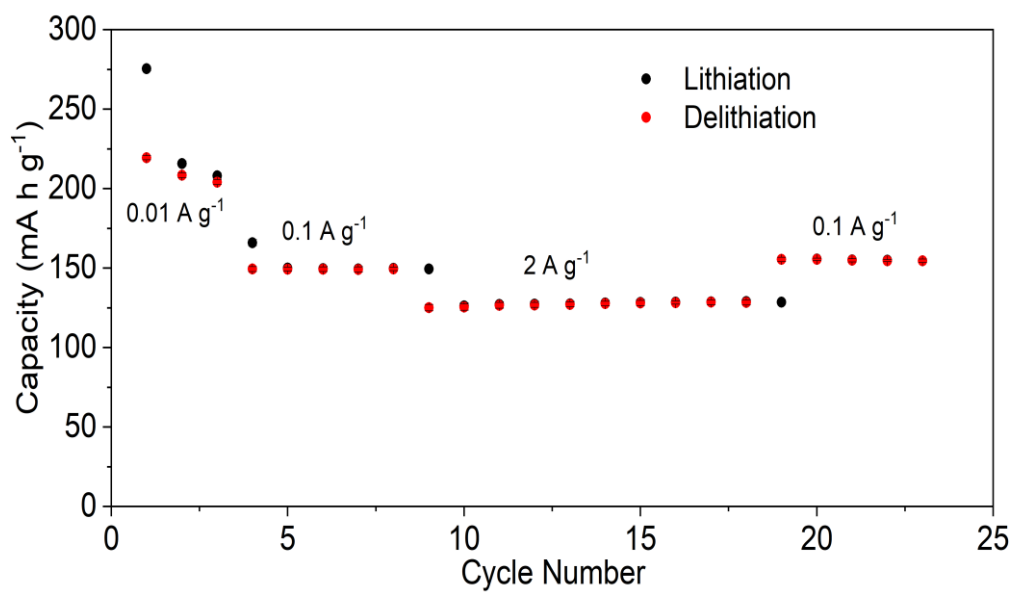
SI Figure 13: Long term cycling data for TTMO71515. 100 cycles were performed at a current density of 0.2 A g⁻¹.



SI Figure 14: XRD pattern of NTMO622 and the observed minor impurity. Tick marks for the $\text{Nb}_9\text{PO}_{25}$ phase (black dashes) have been added.

SI Table 8: The average capacity retention between the 1st and the final (5th) delithiation cycle at different current densities for NTMO65175175.

NTMO65175175				
Current Density (A g^{-1})	C-rate	1 st Cycle (mA h g^{-1})	Final Cycle (mA h g^{-1})	Capacity Retention (%)
0.1	0.3	171 (5)	170 (7)	99
0.2	0.7	160 (8)	161 (2)	99
0.4	1.4	154 (7)	156 (2)	99
0.6	2.1	150 (6)	151 (3)	99
1	3.4	143 (1)	142 (4)	99
2	6.9	138 (3)	138 (4)	100
4	13.8	118 (2)	106 (1)	89
0.1	0.3	264 (50)	167 (1)	55



SI Figure 15: Average specific capacities of two NTMO71515 cells undergoing an alternative formation cycling involving a higher rate step - 3 cycles at 0.01 A g^{-1} , 5 cycles at 0.1 A g^{-1} and finally 10 cycles at 2 A g^{-1} – before going back to 5 cycles at 0.1 A g^{-1} .