Electronic Supplementary Information file (ESI) for

Water-stable O3-type layered Na transition metal oxides enabling environment friendly 'aqueous processing' of electrodes with long-term electrochemical stability

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Table S1. Lattice parameters obtained from Reitveld refinement of the as-synthesised Na- T_M -oxides (*i.e.*, '0.5 Mn / 0 Ti', '0.4 Mn / 0.1 Ti', '0.2 Mn / 0.3 Ti', '0 Mn / 0.5 Ti'), indicated as per Ti-content.

Ti-content (per mole of Na- T_M -oxide)	c-parameter (Å)	a-parameter (Å)	b-parameter (Å)	
0.0	15.91468	2.9574	2.9574	
0.1	15.9345	2.9747	2.9747	
0.3	16.0013	2.9950	2.9950	
0.5	16.0565	3.0140	3.0140	

Table S2. Chemical compositions (as per ICP-AES data) of the as-synthesised Na-T_M-oxides (designated as 'x Mn / y Ti') (*i.e.*, '0.5 Mn / 0 Ti', '0.4 Mn / 0.1 Ti', '0.2 Mn / 0.3 Ti', '0 Mn / 0.5 Ti').

Na-T _M -oxide	Na	Li	Ni	Mn	Ti	Cu	Mg
'0.5 Mn / 0 Ti'	1.09	0.045	0.3	0.49	0	0.096	0.044
'0.4 Mn / 0.1 Ti'	0.96	0.042	0.3	0.39	0.1	0.093	0.048
'0.2 Mn / 0.3 Ti'	0.98	0.042	0.3	0.19	0.29	0.092	0.048
'0 Mn / 0.5 Ti'	0.96	0.042	0.3	0	0.48	0.092	0.048



Fig. S1. X-ray diffraction patterns, along with Rietveld refinements, corresponding to the as-synthesized $Na[Li_{0.05}Ni_{0.3}Mn_xTi_yCu_{0.1}Mg_{0.05}]O_2$ (further designated as 'x Mn / y Ti') (a) '0.5 Mn / 0 Ti', (b) '0.4 Mn / 0.1 Ti', (c) '0.2 Mn / 0.3 Ti', (d) '0 Mn / 0.5 Ti'.



Fig. S2. EDS elemental maps obtained in SEM, showing the distribution of elements, for the as-synthesized 'control' (or no Ti-containing) Na- T_M -oxide (*i.e.*, '0.5 Mn / 0 Ti').



Fig. S3. EDS elemental maps obtained in SEM, showing the distribution of elements, for the as-synthesized fully Ti-substituted (for Mn-ion) Na- T_M -oxide (*i.e.*, '0 Mn / 0.5 Ti').



Fig. S4. Scanning electron micrographs of 'control' (or no Ti-containing) Na-T_M-oxide (*i.e.*, '0.5 Mn / 0 Ti') (a) un-exposed (*i.e.*, as-synthesized) (b) exposed to air for 28 days and (c) soaked in water for 12 h.



Fig. S5. (a) to (c) Cyclic voltammograms (at 0.1 mV/s) corresponding to the first three scans of Na-T_M-oxide electrodes (designated as 'x Mn / y Ti') for (a) '0.5 Mn / 0 Ti' (b) '0.2 Mn / 0.3 Ti' (c) '0 Mn / 0.5 Ti' compositions. (d) Potential vs. specific capacity plots corresponding to the 1st galvanostatic cycles (at C/5) of the Na-T_M-oxide electrodes (prepared using PVDF binder and NMP solvent) for the '0.2 Mn / 0.3 Ti' and '0 Mn / 0.5 Ti' compositions.



Fig. S6. Rate capability plot (*i.e.*, variations in reversible/discharge specific capacity with current densities) for the fully Ti-substituted (for Mn) Na-T_M-oxide (*i.e.*, '0 Mn / 0.5 Ti'), prepared using PVDF as binder and NMP as solvent.



Fig. S7. Ni 2*p* XPS spectra recorded with pristine electrodes of Na-T_M-oxide (designated as 'x Mn / y Ti') for (a) '0.5 Mn / 0 Ti' (b) '0.2 Mn / 0.3 Ti' (c) '0 Mn / 0.5 Ti'. Mn 2*p* XPS spectra recorded with the partially Ti-substituted Na-T_M-oxide (*i.e.*, '0.2 Mn / 0.3 Ti') for (d) pristine electrode and (e) electrode cycled for 100 electrochemical cycles.



Fig. S8. The equivalent circuit used for fitting the EIS data.

This is the most frequently used model for layered T_M -oxide based cathodes. The EIS data was recorded in the frequency range 10 mHz - 10 kHz in Biologic testing machine (BT-810). Depending on the time scales in which the processes take place, the frequency ranges are further divided into high frequency, medium frequency and low frequency regions (from the left to the right of Nyquist plot).

The following is the description of the circuit used to fit the EIS data:

 $\mathbf{R}_{solution}$ (*i.e.*, solution resistance) is the resistance faced by Na-ions when it crosses the electrolyte from one electrode to the other.

 \mathbf{R}_{SEI} (*i.e.*, resistance due to solid electrolyte interface) is the resistance faced by Na-ions while crossing the solid electrolyte interphase (SEI) between the electrode and electrolyte.

C_{SEI} is the capacitance of the SEI due to the charge accumulation at electrode/electrolyte interface.

 \mathbf{R}_{CT} (*i.e.*, charge transfer resistance) refers to the resistance faced by the basic charge transfer at the surface of electrode-active particles.

 C_{DL} is the capacitance associated with the electrochemical double layer on the surface of electrode-active particles.

 Z_w is the Warburg component (*i.e.*, limited diffusion coefficient) associated with the solid-state diffusion of Na-ion in the bulk of the crystal lattice.



Fig. S9. First cycle charge profiles (at C/5) for the three types of electrodes prepared with the optimized '0 Mn / 0.5 Ti' Na-T_M-oxide; *viz.*, '0 Mn / 0.5 Ti' 'aqueous-processed', 'NMP/PVDF-processed' and '0 Mn / 0.5 Ti' – MWCNT 'NMP/PVDF-processed'.



Fig. S10. Potential vs. specific capacity plots corresponding to galvanostatic cycling at C/5 for the fully Tisubstituted (for Mn) Na-T_M-oxide (*i.e.*, '0 Mn / 0.5 Ti') electrodes prepared using 'Na-alginate' as binder and 'water' as solvent (*i.e.*, 'aqueous processed' electrodes) for the (a) 100th, (b) 200th, (c) 300th, (d) 400th, (e) 500th, (f) 600th, (g) 700th and (h) 750th galvanostatic cycles.