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Electronic Supplementary Information

Structural Factors for Activating Anionic Redox in Li-rich Ti-based Cathodes

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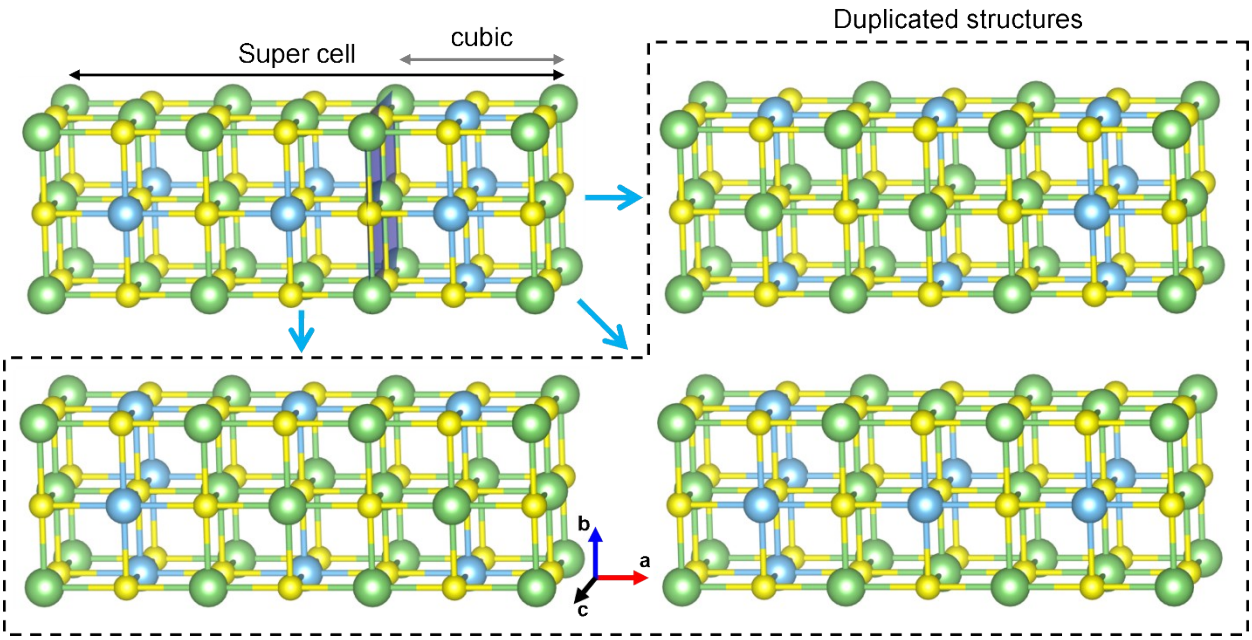

Fig. S1. Elongated supercell rock salt structure of Li_2TiS_3 as an example having same chemical formula as an example of duplicated ion configuration. The base cubic system was designed based on the rocksalt NaCl. We contemplated all possible cation ordering about Li/Ti position and eliminated duplicate structures to make an energy distribution histogram.

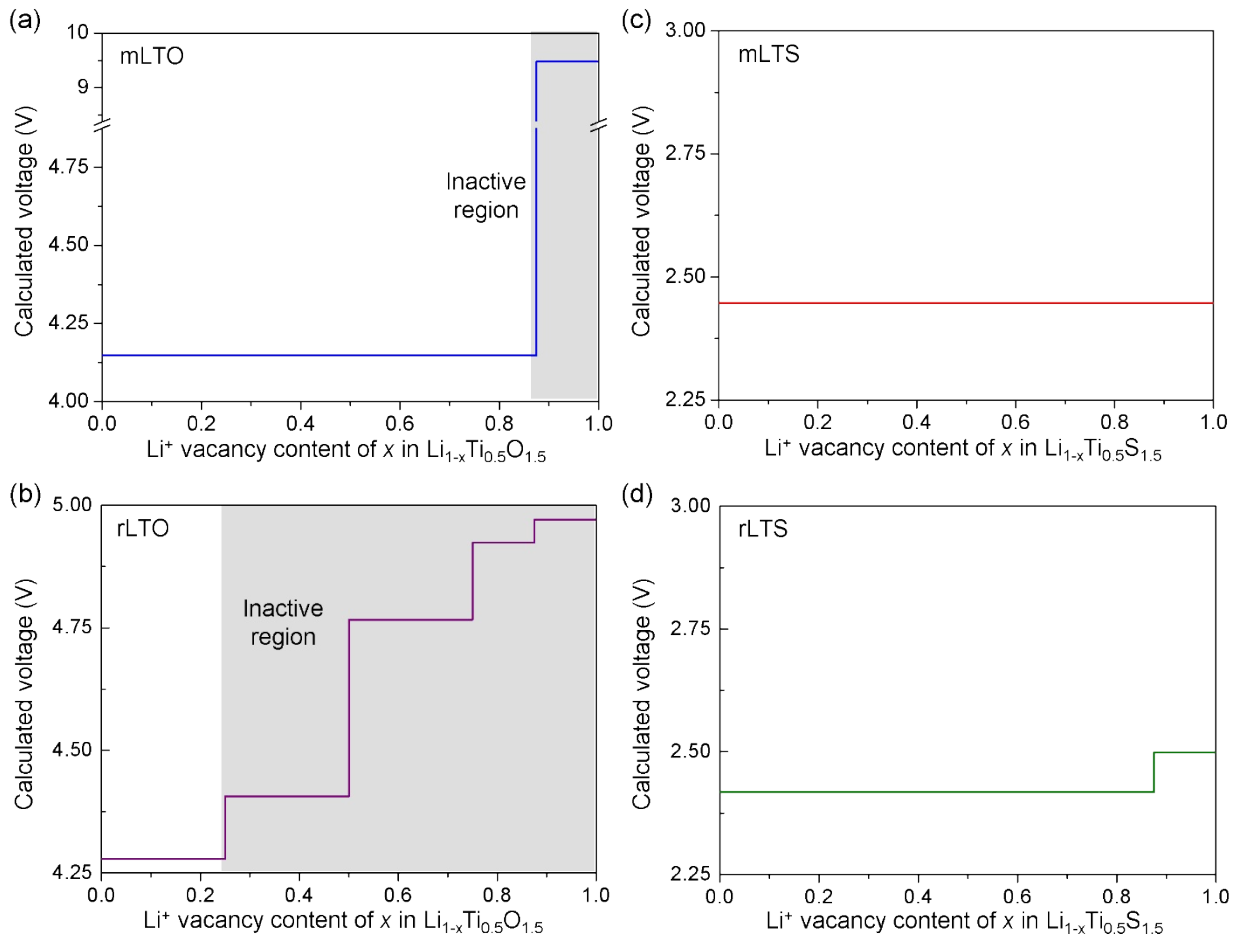

Fig. S2. (a-d) calculated voltages based on the mixing enthalpy as a function of Li ion vacancy content (x) in $Li_{1-x}Ti_{0.5}A_{1.5}$ of 4 systems.

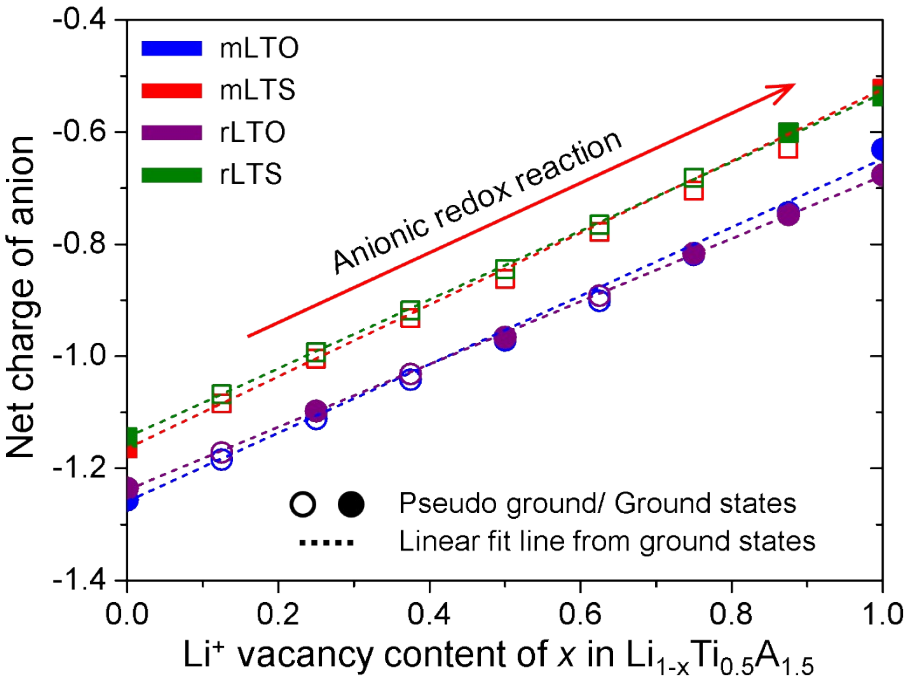

Fig. S3. Bader charge analysis of 4 systems as a function of Li ion vacancy content (x) in $Li_{1-x}Ti_{0.5}A_{1.5}$.

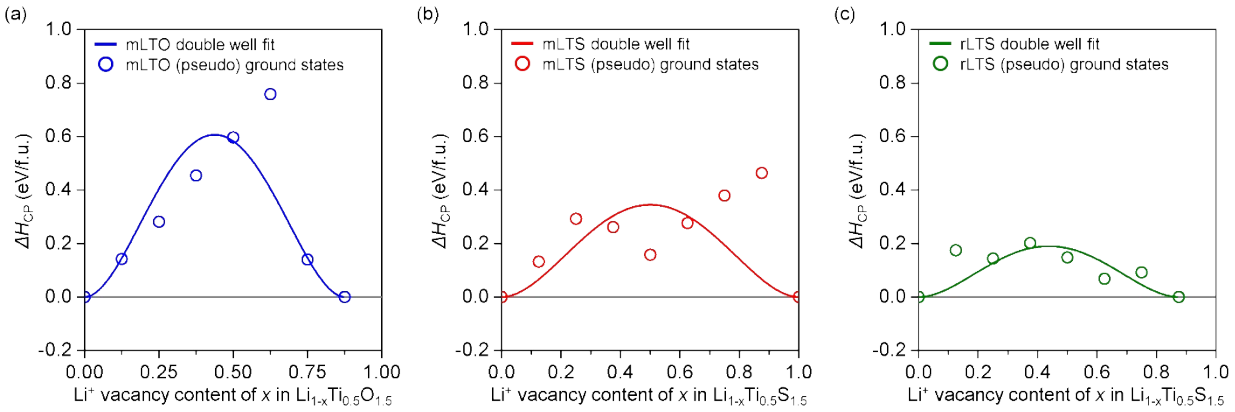

Fig. S4. Combined phase mixing enthalpies of 4 systems. The ΔH_{cp} are fit using quadratic double well function based on ground and pseudo-ground states .

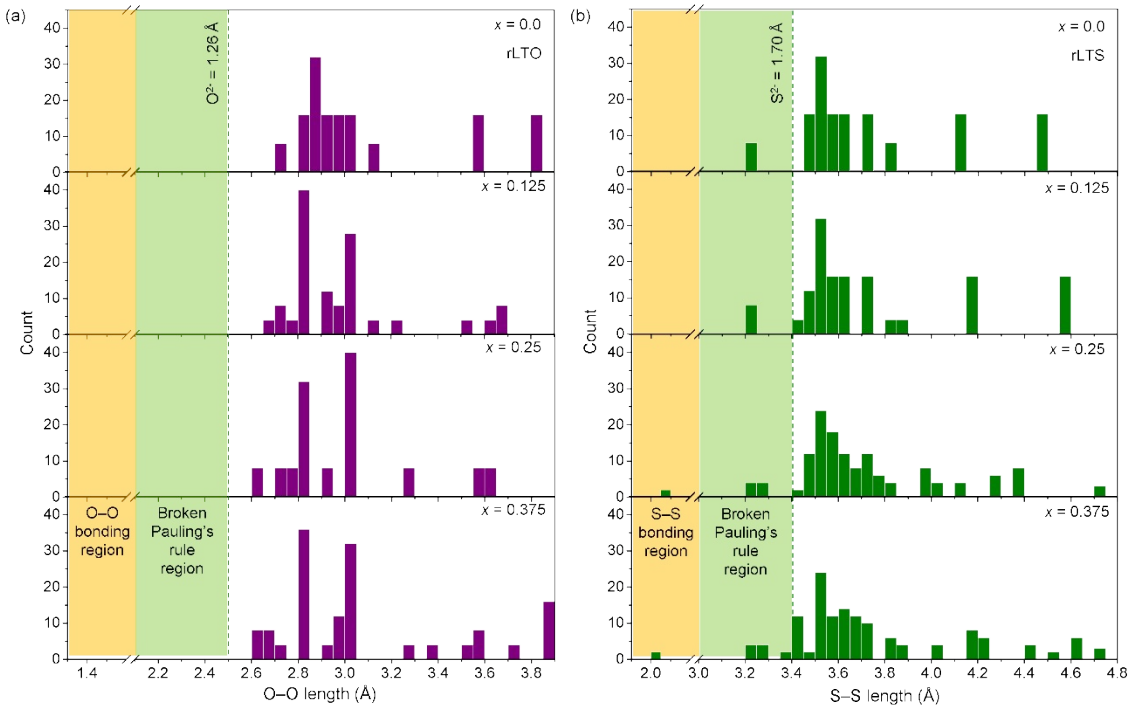

Fig. S5. population of A–A distance of (a) rLTO and (b) rLTS during delithation process till $x = 0.375$ in $Li_{1-x}Ti_{0.5}A_{1.5}$. The green filled region indicates broken structure stability regarding Pauling's rule and anion radius A^{2-} in 6 coordination number and the yellow filled area display chemical bonds evolving between each anion.