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ARTICLE

Electronic Supporting Information (ESI)

Rational Design of Ti-Based Oxygen Redox Layered Oxides for Advanced Sodium-ion Batteries

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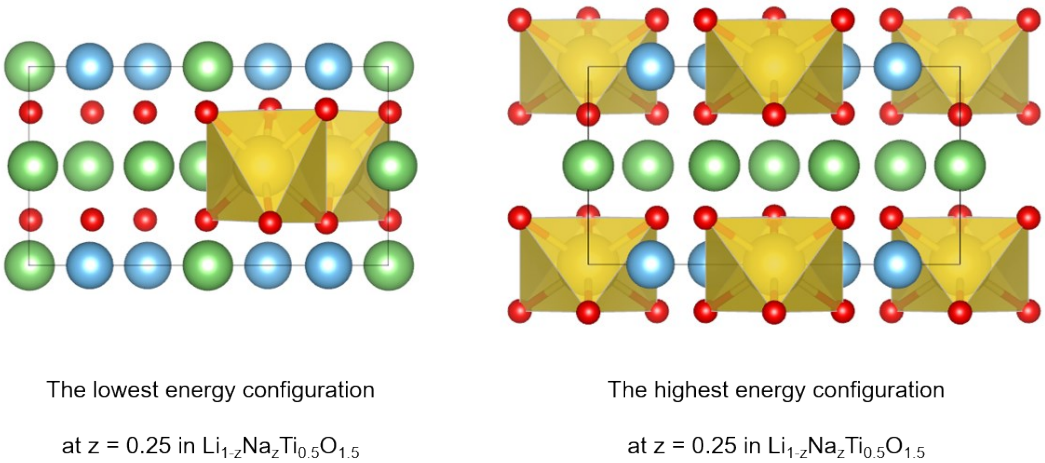

Figure S1. Atomic structures of the lowest (left) and highest (right) energy configuration at $z = 0.25$ in $Li_{1-z}Na_zTi_{0.5}O_{1.5}$, which were obtained from the energy diagram in Figure 2a. Unambiguously, Na ions are not favorable in the 2b site in the thermodynamic point of view.

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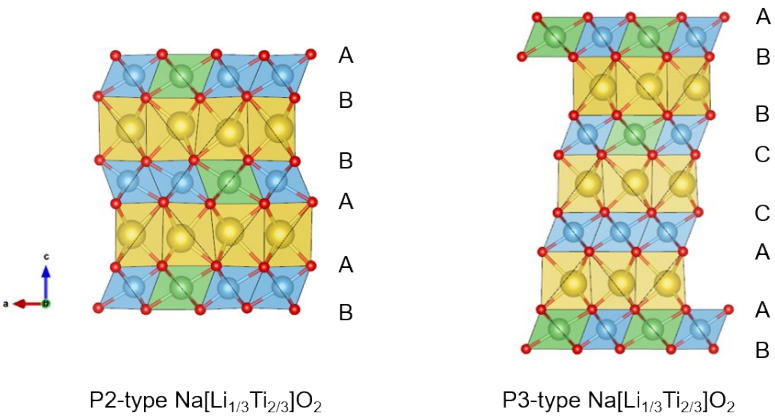

Figure S2. The atomic models of P2-type $Na[Li_{1/3}Ti_{2/3}]O_2$ and P3-NLTO, where P refers to Na ions occupying the prismatic sites between the Ti-containing layers and 2 and 3 mean that two Ti (BA and AB) and three (BAACCB) Ti layers are repeated along the *c*-axis. We calculated relative energy differences ($\Delta E = E_P - E_{O3}$, where P refers to possible phases) between P2-NLTO or P3-NLTO and O3-NLTO for understanding the comparison. Based on the simple equation, ΔE_{P2} and ΔE_{P3} were calculated to be 0.302 eV/f.u. and 0.601 eV/f.u., respectively. This indicates that O3-NLTO phase is the most stable structure as compared with P2-NLTO or P3-NLTO phases. Recently, 'cationic potential ($\Phi_{cation} = \frac{\Phi_M \Phi_{Na}}{\Phi_O}$)' was captured as one of the dominant key factors of Na-based layered materials to predict the stacking sequences.[S1] Φ_{Na} represents the ionic potential of sodium, and this factor increases as sodium content increases which demonstrates that the pristine states of high sodium content materials are expected to be synthesized in O-type stacking. For this reason, the stacking type of sodium layered oxides can be different depending on sodium content and it concurs with some research papers that NLTO shows various phases at pristine state.[S2] These experimental and theoretical studies highly correlate to support the discussion in O3-$Na[Li_{1/3}Ti_{2/3}]O_2$. It can be acceptable to synthesize O3-NLTO phase as we calculated with the most stable structure in the pristine state and the phase of materials can be determined by Na contents.

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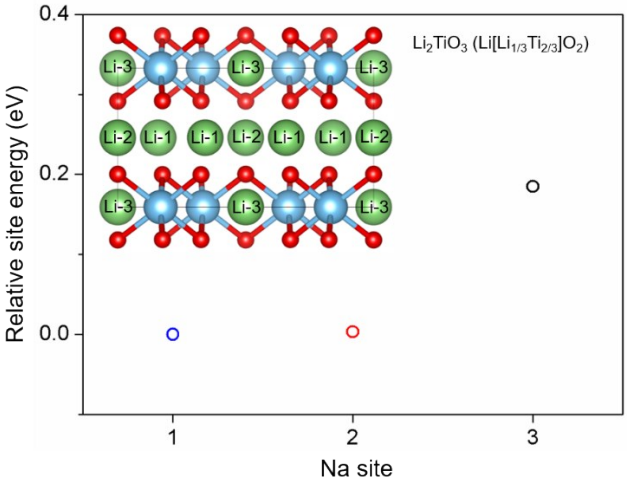

Figure S3. Na relative site energy depending on the Li atoms at the 4h (Li-1), 2c (Li-2), and 2b (Li-3) sites with respect to Wyckoff positions in Li_2TiO_3 (Li: green, Ti: light blue, and O: red).

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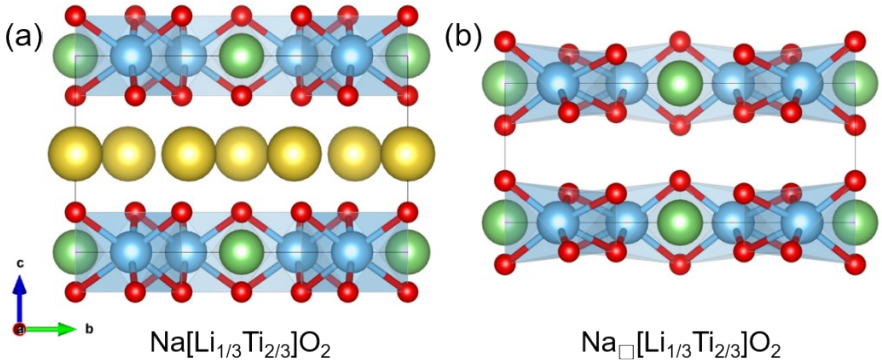

Figure S4. Fully relaxed atomic structures of $Na[Li_{1/3}Ti_{2/3}]O_2$ (left) and $Na_{\square}[Li_{1/3}Ti_{2/3}]O_2$ (right).

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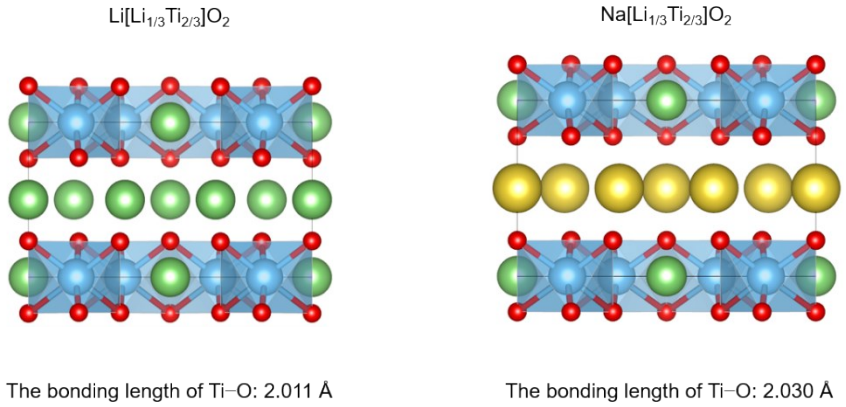

Figure S5. The calculated bonding lengths of Ti–O in $Li[Li_{1/3}Ti_{2/3}]O_2$ and $Na[Li_{1/3}Ti_{2/3}]O_2$ layered oxides.

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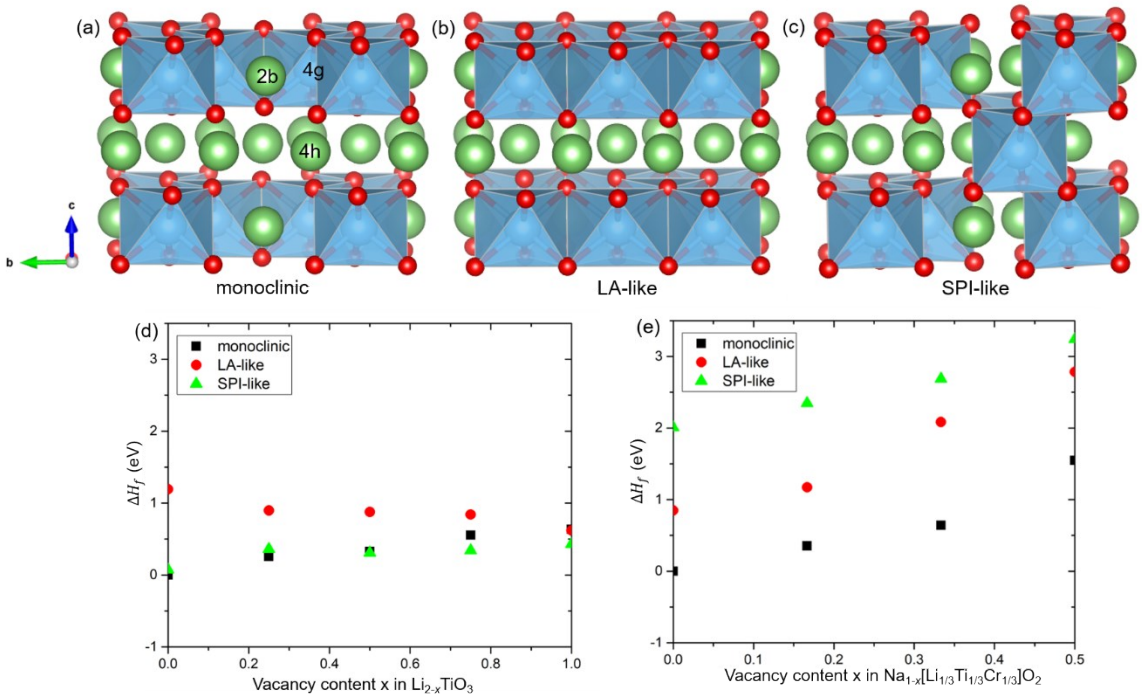

Figure S6. Atomic models of Li_2TiO_3 with (a) monoclinic, (b) densified layered-like (LA-like), and (c) defected spinel-like (SPI-like) and their structures are constructed based on the previous literature.[S3] (d) Relative formation energies as a function of vacancy content (*x*) in $Li_{2-x}TiO_3$ for $0.0 \leq x \leq 1.0$) and (e) those in $Na_{1-x}[Li_{1/3}Ti_{1/3}Cr_{1/3}]O_2$. To confirm the inter- and intra-layer Ti migrations in $Li_{2-x}TiO_3$, we adopted the two-type Ti migration paths: i) 4g site → 4h site (denoted as interlayer migration) and ii) 4g site → 2b site (denoted as intra-layer migration), which have been accepted as general transition metal migration pathways in Li-excess layered oxides. The path-i refers to the LA-like structure and the path-ii corresponds to the SPI-like structure. The values of formation energies were calculated according to the equation as below.

$$\Delta H_f = E_{(Li_{2-x}TiO_3)} - \left(1 - \frac{x}{2}\right) E_{(Li_2TiO_3)^{monoclinic}} - \frac{x}{2} E_{(Li_0TiO_3)^{SPI\text{-}like}}$$

, where E is the system total energy and *x* refers to vacancy content. Figure S6 shows the monoclinic structure is thermodynamically more stable than the rest two structure modes until $x = 0.5$ but the SPI-like one is more favourable for a value above $x = 0.5$. These results imply that the possible path of Ti ions in Li_2TiO_3 is the interlayer migration from the $[Li_{1/3}Ti_{2/3}]O_2$ layer to the LiO_2 layer rather than the intralayer one. Additionally, Figure S6e presents that we calculated the formation energies as a function of vacancy content from $x = 0.0$ to $x = 0.5$ in $Na_{1-x}[Li_{1/3}Ti_{1/3}Cr_{1/3}]O_2$ (NLTCO). Unlike $Li[Li_{1/3}Ti_{2/3}]O_2$, the SPI-like structure in NLTCO is not thermodynamically favourable at $x = 0.5$ even that is much more stable than the rest two structure models. From this result, we speculate that the interlayer migration of Ti ions does not occur during the desodiation process.

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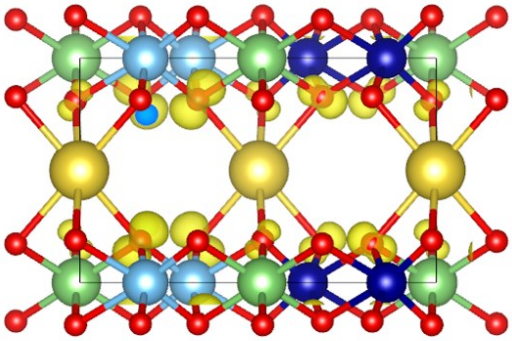

Figure S7. Spatial electron distribution in the valence band from −1 to 0 eV at x = 0.667 in $Na_{1-x}[Li_{1/3}Ti_{1/3}Cr_{1/3}]O_2$. There are no Cr and Ti 3*d*-electron, whereas lone-pair oxygen 2*p*-electron is dominantly present in the desodiated oxide.

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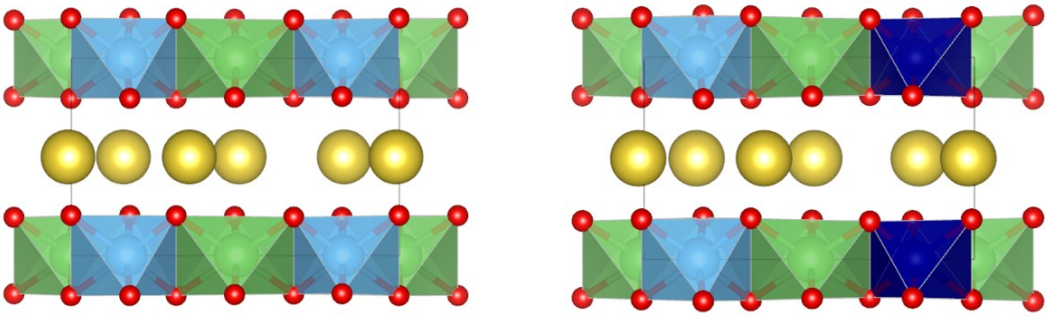

x = 1/6 in $Na_{1-x}[Li_{1/3}Ti_{2/3}]O_2$

Structural formation energy: -0.1858 eV

x = 1/6 in $Na_{1-x}[Li_{1/3}Ti_{1/3}Cr_{1/3}]O_2$

Structural formation energy: -0.0666 eV

Figure S8. Atomic structures of $Na_{1-x}[Li_{1/3}Ti_{2/3}]O_2$ (left) and $Na_{1-x}[Li_{1/3}Ti_{1/3}Cr_{1/3}]O_2$ (right) at $x = 1/6$. The structural formation energy ($E_{SF} = E_{FR} - E_{RB}$) was calculated from the total energy difference between fully relaxed (E_{FR}) and rigid body (E_{RB}) models. The lower value of E_{SF} in $Na_{1-x}[Li_{1/3}Ti_{1/3}Cr_{1/3}]O_2$ than that in $Na_{1-x}[Li_{1/3}Ti_{2/3}]O_2$ indicates the reduced phase change by the Na-extraction.

Reference

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[S2] G. V. Shilov, V. B. Nalbandyan, V. A. Volochaev and L. O. Atovmyan, *Int. J. Inorg. Mater.*, 2000, **2**, 443–449.

[S3] J. -M. Lim, D. Kim, Y.-G. Lim, M.-S. Park, Y.-J. Kim, M. Cho and K. Cho, J. Mater. Chem. A, 2015, 3, 7066–7076.

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