Supporting Information

Ti substituted Li[Li_{0.26}Mn_{0.6-x}Ti_xNi_{0.07}Co_{0.07}]O_2 layered cathode material with improved structural stability and suppressed voltage fading

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Supporting information includes the following contents:

- XRD rietveld refinement
- Details of first-principles and phonon calculations
- Results of first-principles and phonon predictions
- Figures and tables for supporting information
- References for supporting information
**Figure S1**: XRD Rietveld refinement of (a) Li[Li_{0.26}Mn_{0.6}Ni_{0.07}Co_{0.07}]O_{2}; (b) Li[Li_{0.26}Mn_{0.563}Ti_{0.037}Ni_{0.07}Co_{0.07}]O_{2}; (c) Li[Li_{0.26}Mn_{0.526}Ti_{0.074}Ni_{0.07}Co_{0.07}]O_{2}. (Red points correspond to the experimental data, black lines are the calculated patterns, blue lines are the difference between the calculated and experimental patterns and the vertical green bars correspond to the expected positions of Bragg reflections of Li_{1.33}Mn_{0.67}O_{2}, vertical orange bars to Si.)
In the present work, all density functional theory (DFT) based first-principles calculations are performed using the VASP 5.3 software, with the ion-electron interaction depicted by the projector augmented wave (PAW) method. The exchange-correlation (X-C) functional is described by an improved generalized gradient approximation (GGA) for densely packed solids and their surfaces (PBEsol). In general, PBEsol predicts properties in the middle of the widely used GGA and the local density approximation (LDA), and gives a good account of thermal properties for Li-ion battery materials. In order to take into consideration the strong on-site Coulomb interaction (\( U \)) presented in the localized 3d electrons of magnetic elements Mn, Co, and Ni, the PBEsol+\( U \) calculations are performed for the layered Li-ion cathode materials \( \text{Li}_9(\text{X}_1\text{Y}_1\text{Z}_1\text{Mn}_6)\text{O}_{18} \) (X, Y, and Z = Co, Li, Mn, Ni, and Ti) as well as their endmember compounds \( \text{Li}_9(\text{M}_9)\text{O}_{18} \) (M = Co, Li, Mn, Ni, and Ti) according to the approach of Liechtenstein et al. The effective Coulomb interaction \( U_{\text{eff}} = U - J \) is adopted herein with the screened exchange energy \( J \) fixed at 1 eV. In the present work, \( U_{\text{eff}} = 4.5, 5.7, \) and 5.1 eV are used for Mn, Co, and Ni, respectively, according to the previous first-principles practices for Li-ion battery materials. For each element in \( \text{Li}_9(\text{X}_1\text{Y}_1\text{Z}_1\text{Mn}_6)\text{O}_{18} \), three electrons are used as valences for Li (1\( s^22s^1 \)), six for O (2\( s^22p^4 \)), seven for Mn (3\( d^54s^2 \)), nine for Co (3\( d^74s^2 \)), ten for Ni (3\( d^84s^2 \)), and ten for Ti (3\( p^63d^24s^2 \)). During VASP calculations, a 36-atom supercell with 12 layers and 3 atoms on each layer is used (see Figure S2). In addition, a 520 eV plane wave energy cutoff and a 7×7×2\( k \)-point mesh are employed. The reciprocal-space energy integration is performed by the Gaussian smearing method. The energy convergence criterion of electronic self-consistency is chosen as at least 10\(^{-6} \) eV per atom. Note that (i) the final calculations to get accurate total energy (as well as force constants, see below) are also performed by the Gaussian smearing method, and (ii) the total energy for a free atom is calculated using a large orthorhombic cell with the lattice parameters of (20×22×24 Å), together with the spin polarization included and only the \( \Gamma \)-center \( k \)-point mesh employed.

After first-principles calculations, equilibrium properties for the structure of interest are determined by fitting the first-principles energy versus volume data points (usually nine data points employed for each structure in the present work) according to a four-parameter Birch-Murnaghan equation of state (EOS).
\[ E^a(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2} \]  
(S1)

where, \( a, b, c, \) and \( d \) are fitting parameters. Equilibrium properties resulted from this EOS include volume \((V_0)\), energy \((E_0)\), bulk modulus \((B_0)\) and its pressure derivative \((B_0')\).\(^9\)

In order to verify structural stability of Li\(_9\)(X\(_1\)Y\(_1\)Z\(_1\)Mn\(_6\))O\(_{18}\), phonon calculations are performed using the supercell method.\(^10\) The 144-atom supercell is used, which is a (2\(\times\)2\(\times\)1) supercell with respect to the previous 36-atom cell. Force constants, i.e., the Hessian matrix, are calculated in real space using again the VASP 5.3 code by means of a 2\(\times\)2\(\times\)1 \(k\)-point mesh and the same settings mentioned above. Phonon properties are calculated by the YPHON code:\(^11, 12\) a parameter-free, mixed-space approach developed recently in our group. More detail of phonon calculations using YPHON can be found in other publications.\(^5, 6, 11-13\)

**RESULTS OF FIRST-PRINCIPLES AND PHONON PREDICTIONS**

Regarding the 36-atom supercell of Li\(_9\)(X\(_1\)Y\(_1\)Z\(_1\)Mn\(_6\))O\(_{18}\), six independent structures exist due to the distribution of X, Y, and Z within the metal-sublattice. Test calculations are performed for all these six structures with X=Li, Y=Co, and Z=Ni, the predicted (relative) total energies are plotted in Figure S2 with respect to the degree of dispersion of different metals (cations) within the metal-sublattice. It is found that distributions of X, Y, and Z on different layers result in lower energies (str5 and str6 in Figure S2). In addition, the distances between X-Y (Li-Co) and X-Z (Li-Ni) in str6 are obviously longer than those in str5. The same as our previous findings,\(^14\) the distributions of X, Y, and Z within the metal-sublattice follow the maximum entropy probability distribution (MEPD), with the same kind of element as far (dispersion) as possible. str6 is therefore the present selection to study the layered cathode materials Li\(_9\)(X\(_1\)Y\(_1\)Z\(_1\)Mn\(_6\))O\(_{18}\).

Figure S3 illustrates the cohesive energies of Li\(_9\)(M\(_9\))O\(_{18}\) and Li\(_9\)(X\(_3\)Mn\(_6\))O\(_{18}\) as a function of volume and bulk modulus with and without the effect of \(U_{\text{eff}}\) (data are listed in Table 1). The conclusions from this figure are shown in the main text part.

Figure S4 illustrates the predicted phonon densities of state (DOS) for LiCoO\(_2\) and Li\(_9\)(Ti\(_1\)Co\(_1\)Ni\(_1\)Mn\(_6\))O\(_{18}\) by PBEsol+\(U_{\text{eff}}\) at their equilibrium volume (see Table 1 for details). It is seen that the predicted phonon DOS of LiCoO\(_2\) agree reasonably well with the measured
neutron-weighted phonon DOS.\textsuperscript{15} Phonon DOS of Li\textsubscript{9}(Ti\textsubscript{1}Co\textsubscript{1}Ni\textsubscript{1}Mn\textsubscript{6})O\textsubscript{18} shows broader feathers compared with that of LiCoO\textsubscript{2} due to multi-component metals existed in the metal-sublattice.\textsuperscript{16}

Figure S5 plots the key stretching force constants of LiNiO\textsubscript{2} between each atomic pair predicted by PBEsol+\textit{U}\textsubscript{eff}. The large but negative stretching force constants (near 6 eV/Å\textsuperscript{2}) are between the O-O atomic pairs (such as atom pair 1-3 as shown in the figure), which is main reason for the instability of this structure under PBEsol+\textit{U}\textsubscript{eff}. Note that PBEsol will predict a stable structure of LiNiO\textsubscript{2}, see Table 1.

Figure S6 shows the differential change density with respect to the corresponding free atoms and the magnetism change density (spin up minus spin down) for Li\textsubscript{9}(Ti\textsubscript{1}Co\textsubscript{1}Ni\textsubscript{1}Mn\textsubscript{6})O\textsubscript{18} predicted by PBEsol+\textit{U}\textsubscript{eff}. It is also found that Li\textsubscript{9}(Ti\textsubscript{1}Co\textsubscript{1}Ni\textsubscript{1}Mn\textsubscript{6})O\textsubscript{18} is a compound with a mixing of ionic bonds without obvious directionality (mainly O-Mn and O-Ti) and covalent bonds with clear directionality (O-Co and especially O-Ni).

Table S1 summarizes the Raman and infrared (IR) phonon frequencies at the \textit{\Gamma} point of LiCoO\textsubscript{2} predicted by the PBEsol+\textit{U}\textsubscript{eff} method. Our predictions agree well with the Raman measurements,\textsuperscript{17, 18} and agree reasonable well with the IR measurements.\textsuperscript{17, 19} Note that the Raman measurements are more accurate than those from the IR measurements due to the broader IR spectra.\textsuperscript{17}
FIGURES AND TABLES FOR SUPPORTING INFORMATION

Figure S2: Phase stability of Li$_9$(Li$_{1}$Co$_{1}$Ni$_{1}$Mn$_{6}$)O$_{18}$ (here, X = Li) as a function of cation(metal) dispersion within the metal-sublattice. The number above each structure indicates different structure (i.e., str1, str2, ..., and str6).

Figure S3: Cohesive energies of Li$_9$(M$_9$)O$_{18}$ and Li$_9$(X$_1$Y$_1$Z$_1$Mn$_{6}$)O$_{18}$ as a function of volume (a) and bulk modulus (b) predicted by PBEsol with and without the effect of $U_{\text{eff}}$. Data are shown in Table 1.
**Figure S4:** Predicted phonon densities of state (DOS) for LiCoO$_2$ and Li$_6$(Ti$_1$Co$_1$Ni$_1$Mn$_6$)O$_{18}$ by PBEsol+$U_{\text{eff}}$, in comparison with the measured neutron-weighted phonon DOS of LiCoO$_2$.\textsuperscript{15} Note that integration of phonon DOS is same for each structure.

**Figure S5:** Key stretching force constants of LiNiO$_2$ between each atomic pair predicted by PBEsol+$U_{\text{eff}}$. 
Figure S6: (a) Change density difference with respect to the corresponding free atoms (only change losses are shown, and the isosurface is plotted at 1/3 of the maximum value), and (b) magnetism change density (spin up minus spin down, and the isosurface is plotted at 1/5 of the maximum value). Predictions are performed by PBEsol+$U_{\text{eff}}$ for Li$_9$(Ti$_1$Co$_1$Ni$_1$Mn$_6$)O$_{18}$.

Table S1. Raman and infrared (IR) phonon frequencies (cm$^{-1}$) at the $\Gamma$ point of LiCoO$_2$ predicted by the PBEsol+$U_{\text{eff}}$ method in comparison with experimental data. Note that the Raman measurements are more accurate than those from the IR measurements due to the broader IR spectra.

<table>
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<th>Mode</th>
<th>$A_{2u}$ (IR)</th>
<th>$A_{1g}$ (Raman)</th>
<th>$E_u$ (IR)</th>
<th>$E_g$ (Raman)</th>
<th>$A_{2u}$ (IR)</th>
<th>$E_u$ (IR)</th>
</tr>
</thead>
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<tr>
<td>This work</td>
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<td>607</td>
<td>564</td>
<td>506</td>
<td>490</td>
<td>325</td>
</tr>
<tr>
<td>Expt.</td>
<td>596 (665$^a$)$^b$</td>
<td>595$^b$</td>
<td>555$^b$</td>
<td>485$^b$</td>
<td>508$^b$</td>
<td>265$^b$</td>
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<tr>
<td></td>
<td>600 (650)$^c$</td>
<td>597$^d$</td>
<td>570$^c$</td>
<td>487$^d$</td>
<td>447$^c$</td>
<td>267$^c$</td>
</tr>
</tbody>
</table>

$^a$Shoulder of the peak at 596 or 600 cm$^{-1}$.
$^b$Raman and IR measurements.$^{17}$
$^c$IR measurements.$^{19}$
$^d$Raman measurements.$^{18}$

**REFERENCES FOR SUPPORTING INFORMATION**