Supporting Information

Impact of trace extrinsic defect formation on the symmetry transition in spinel LiNi$_{0.5}$Mn$_{1.5}$O$_{4-\delta}$ and their electrochemical characteristics

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A schematic illustration of the metal excess model is shown in Fig. S1. The defect formation energy in metal excess models is expressed with Kröger-Vink:

\[
\begin{align*}
\frac{1}{4}(\text{LiNi}_{0.5-x}\text{Mn}_{1.5}M_x\text{O}_4) & \rightarrow \left(\text{Li}_i^+ + \left(\frac{1}{2} - x\right)\text{Ni}^{3-} + \frac{3}{2}\text{Mn}^{4-} + x\text{M}_i^+ + 8e^- + 2\text{O}_2\right) \\
\frac{1}{4}(\text{LiNi}_{0.5}\text{Mn}_{1.5-y}M_y\text{O}_4) & \rightarrow \left(\text{Li}_i^+ + \frac{1}{2}\text{Ni}_i^{3-} + \left(\frac{3}{2} - y\right)\text{Mn}^{4-} + y\text{M}_i^{3-} + 8e^- + 2\text{O}_2\right)
\end{align*}
\]

(S1) (S2)

The defect generation energy can be expressed with the equations (1) and (2) in the main text using the total energy $E (X)$ obtained by the first principles calculation.

Effects of transition metal substitution on the Ni$^{2+}$/Mn$^{4+}$ ordering

Two different types of oxygen defect models, an oxygen vacancy model and metal-excess model, were used for the calculations. Oxygen vacancies occupied at nearest neighbor oxygen sites from substituted metals in the oxygen vacancy model. The oxygen vacancy formation energies for $P4_332$ and $Fd-3m$ LiNi$_{0.375}$Mn$_{1.25}$O$_4$ and LiNi$_{0.375}$Mn$_{1.25}$O$_4$ (M = Ti, V, Cr, Fe, Co, Cu, Zn, Sn) are summarized in Supplementary Figure S1. From the crystallographic features, oxygen atoms included in both $P4_332$ and $Fd-3m$ type symmetries have two possible spatial
configurations: coordinated with one Ni atom and two Mn atoms, or coordinated with three Mn atoms. A series of 
$\text{LiNi}_{0.375}\text{Mn}_{1.5}M_{0.125}\text{O}_4$ derivatives showed higher formation energies than those of $\text{LiNi}_{0.5}\text{Mn}_{1.375}M_{0.125}\text{O}_4$ compounds independent of the transition metal type. Since the formation of lattice defects as described by $M_{\text{Ni2+}}$ simultaneously generates $\text{Mn}^{3+}$ and $M_{\text{Mn4+}}$ lattice defects due to corresponding charge neutralization, oxygen vacancy-free $\text{LiNi}_{0.375}\text{Mn}_{1.5}M_{0.125}\text{O}_4$ compounds are considered to be less stable. In contrast, the oxygen vacancy formation energies for the incorporation of $\text{Fe}_{\text{Mn4+}}$, $\text{Cu}_{\text{Ni}}$, $\text{Cu}_{\text{Mn4+}}$, and $\text{Zn}_{\text{Mn4+}}$, were significantly lower than stoichiometric $\text{LiNi}_{0.375}\text{Mn}_{1.5}\text{O}_4$. In particularly, divalent $\text{Cu}^{2+}_{\text{Mn}}$ and $\text{Zn}^{2+}_{\text{Mn}}$ can be preferentially incorporated at oxygen vacancy sites without $\text{Mn}^{3+}$ formation.

We further considered the effects of Frenkel defects, in which transition metals occupy interstitial sites, by using the metal-excess model for DFT calculations. The positions of two neighboring tetrahedral Li ions are assumed to migrate to octahedral vacancy sites, as shown in Supplementary Figure S2(a); this is the most stable cationic arrangement for interstitial Ni and Mn. Defect formation energies for the metal-excess model for $\text{LiNi}_{0.5-x}\text{Mn}_{1.5}M_x\text{O}_4$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5-y}M_y\text{O}_4$ ($0 \leq x \leq 0.125, 0 \leq y \leq 0.125, M = (b) \text{Ti}, (c) \text{V}, (d) \text{Cr}, (e) \text{Fe}, (f) \text{Co}, (g) \text{Cu}, (h) \text{Zn}, (i) \text{Sn}$) with $P4_332$ and $Fd-3m$ type symmetries were summarized in Supplementary Figure S2(b-i). As in the case of the stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, the defect formation energy of the $Fd-3m$ type structure was lower than that of the $P4_332$ structure, independent of the transition metal cation inducing the extrinsic defect formation. We further evaluated antisite defect formation energies for the substituted transition metals and neighboring Ni/Mn in both $P4_332$ and $Fd-3m$, as shown in Supplementary Figure S3. The Ni or Mn sites forming the antisite defects are spatially distinguished by the difference in the point-to-point sharing and the edge sharing with the Li octahedron. Two different Ni sites (P - Mn

1, P - MNi 2) and two Mn sites (P - MMn 1, P - MMn 2) are possible in the $P4_332$ structure, and one possible Ni site (F - MNi) and three Mn sites (F - MMn 1, F - MMn 2, F - MMn 3) exists in the $Fd-3m$ structure, respectively. Our calculations imply that Ti, V, Cr, Fe, Co, Sn cations preferentially occupy Mn sites, forming extrinsic defects ($^{\text{Ti}}_{\text{Mn}}$, $^{\text{V}}_{\text{Mn}}$, $^{\text{Cr}}_{\text{Mn}}$, $^{\text{Fe}}_{\text{Mn}}$, $^{\text{Co}}_{\text{Mn}}$, $^{\text{Sn}}_{\text{Mn}}$) compared to the occupation of interstitial sites (Frenkel defects). In contrast, Cu$^{2+}$ favorably occupied interstitial sites ($^{\text{Cu}}_{\text{int}}$). We estimated the energy for disordering Ni/Mn arrangements caused by the penetration of transition metals into interstitial sites (Supplementary Figure S4). This implies that the Ni/Mn disordering was highly promoted due solely to Cu substitution according to negative antisite energy.
Supplementary Figure S1

Schematic illustration of metal-excess model for LiNi_{0.5}Mn_{1.5-y}M_yO_{4-d}.
Supplementary Figure S2

Oxygen vacancy formation energies for stoichiometric LiNi$_{0.5}$Mn$_{1.5}$O$_4$ with $P4_332$ and $Fd-3m$ type symmetries.
Supplementary Figure S3

(a) Schematic illustration of positional transitions in two neighboring tetrahedral Li ions to octahedral vacancy sites, and defect formation energies for metal-excess model for LiNi$_{0.5}$Mn$_{1.5}$M$_x$O$_4$ and LiNi$_{0.5}$Mn$_{1.5-y}$M$_y$O$_4$ ($0 \leq x \leq 0.125$, $0 \leq y \leq 0.125$, $M =$ (b) Ti, (c) V, (d) Cr, (e) Fe, (f) Co, (g) Cu, (h) Zn, (i) Sn) with $P4_332$ and $Fd-3m$ type symmetries.
Supplementary Figure S4

Atomic arrangement of nearest neighbor (NN) Ni/Mn around incorporated extrinsic interstitial metal (a) in \( P4_332 \), and (b), (c) in \( Fd-3m \) type structures. Possible antisite defects for the interstitial metal and NN Ni/Mn are described in the illustrations by the arrows. Corresponding antisite defect formation energies in both (d) \( P4_332 \) and (e) \( Fd-3m \)
Supplementary Figure S5

Antisite defect formation energies for the substituted transition metal and neighboring Ni in LiNi_{0.5}Mn_{1.5}O_4 with \( P4_332 \) symmetry
Supplementary Figure S6

Powder XRD profiles and Rietveld refinement results of the Cu-incorporated LiNi$_{0.5}$Mn$_{1.5}$O$_{4-\delta}$ derivative crystals.

<table>
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<th>Site</th>
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<th>$y$</th>
<th>$z$</th>
<th>$g$</th>
<th>$B$</th>
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<td>0.000(-)</td>
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<td>1(-)</td>
<td>1(-)</td>
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<td>0.625</td>
<td>0.625</td>
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<tr>
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<td></td>
<td></td>
<td></td>
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<tr>
<td>12d</td>
<td>Mn</td>
<td>0.125</td>
<td>0.3709(8)</td>
<td>0.8791(-)</td>
<td>1.0(1)</td>
<td>0.5(1)</td>
</tr>
<tr>
<td></td>
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<td>8c</td>
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<tr>
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<td>0.87(2)</td>
<td>0.3(1)</td>
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$R_{wp} = 3.403\%$, $R_p = 2.692\%$, $R_o = 3.395\%$, $S = 1.003$, $a = 8.1691(1)$ Å
Supplementary Figure S7

(a) Third cycle charge–discharge profiles at a current density corresponding to 0.2 C at room temperature of
LiNi_{0.5}Mn_{1.5}O_{4-δ}/Li and LiNi_{0.5}Zn_{0.01}Mn_{1.49}O_{4-δ}/Li cells. (b) Raman shift of LiNi_{0.5}Mn_{1.5}O_{4-δ} and
LiNi_{0.5}Mn_{1.49}Zn_{0.01}O_{4-δ}. (c) The calculated Li/M Antisite defect formation energies of LiNi_{0.5}Mn_{1.5}O_{4-δ} and
LiNi_{0.5}Mn_{1.49}Zn_{0.01}O_{4-δ}.

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<tr>
<th>Li/M antisite energy (eV)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Zn</td>
<td>0.05</td>
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</table>

(a) Third cycle charge–discharge profiles at a current density corresponding to 0.2 C at room temperature of
LiNi_{0.5}Mn_{1.5}O_{4-δ}/Li and LiNi_{0.5}Zn_{0.01}Mn_{1.49}O_{4-δ}/Li cells. (b) Raman shift of LiNi_{0.5}Mn_{1.5}O_{4-δ} and
LiNi_{0.5}Mn_{1.49}Zn_{0.01}O_{4-δ}. (c) The calculated Li/M Antisite defect formation energies of LiNi_{0.5}Mn_{1.5}O_{4-δ} and
LiNi_{0.5}Mn_{1.49}Zn_{0.01}O_{4-δ}.
Supplementary Figure S8

(a) Formation energies for the most stable Li/vacancy arrangement and (b) theoretical voltage slope as a function of $z$ in $\text{Li}_{1-z}\text{Ni}_{0.5}\text{Mn}_{1.375}\text{Cu}_{0.125}\text{O}_{3.875}$.

Supplementary Figure S9

Atomic valence distribution near the $\text{Cu}^{2+}$ and oxygen vacancies in (a) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$, (b) $\text{LiNi}_{0.5-x}\text{Mn}_{1.5}\text{Cu}_{x}\text{O}_{4-\delta}$, and (c) $\text{LiNi}_{0.5}\text{Mn}_{1.5-y}\text{Cu}_{y}\text{O}_{4-\delta}$. 
Supplementary Table S1
Chemical compositions of LiNi$_{0.5}$Mn$_{1.5}$O$_{4-x}$ and Cu-incorporated derivative crystals, as evaluated by inductively coupled plasma optical emission spectrometry.

<table>
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<th align="right">Li  :</th>
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<th align="right">Cu  :</th>
<th align="right">Mn  :</th>
</tr>
</thead>
<tbody>
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<td>Cu-incorporated</td>
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<td align="right">0.02 :</td>
<td align="right">2.98 :</td>
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<td align="right"></td>
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<td align="right"></td>
</tr>
<tr>
<td>LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_{4-\delta}$</td>
<td align="right">1.96 :</td>
<td align="right">1    :</td>
<td align="right">-    :</td>
<td align="right">3.02 :</td>
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