Supporting Information

Exploring the origin of electrochemical performance of Cr-doped LiNi$_{0.5}$Mn$_{1.5}$O$_4$

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Computational details

Defect formation energy

In the case of Cr doping, all possible conditions of one Cr atom substituted one TM (Ni or Mn) atom are considered in $P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and $F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$. In more detail, in $P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Cr atom substituted Ni atom in 4b or substituted Mn atom in 12d. In $F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, considering the 4 Ni atoms and 12 Mn atoms are inequivalent each other. 4 different configurations with Cr substitute Ni and 12 different configurations with Cr substitute Mn are considered. And the lowest-energy configurations of Cr$\text{Ni}$-$P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Cr$\text{Ni}$-$F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Cr$\text{Mn}$-$P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, and Cr$\text{Mn}$-$F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$ are shown in Fig S1.

The defect formation energy $E_{\text{def}}$ for Cr substitute Ni is defined as:

$$E_{\text{def}} = E(\text{Li}_8\text{CrNi}_3\text{Mn}_{12}\text{O}_{32}) - E(\text{Li}_8\text{Ni}_4\text{Mn}_{12}\text{O}_{32}) - \mu(\text{Cr}) + \mu(\text{Ni})$$

The defect formation energy $E$ for Cr substitute Mn is defined as:

$$E_{\text{def}} = E(\text{Li}_8\text{CrNi}_4\text{Mn}_{11}\text{O}_{32}) - E(\text{Li}_8\text{Ni}_4\text{Mn}_{12}\text{O}_{32}) - \mu(\text{Cr}) + \mu(\text{Mn})$$

where $E(\text{Li}_8\text{CrNi}_3\text{Mn}_{12}\text{O}_{32})$ is the total energy of Li$_8$CrNi$_3$Mn$_{12}$O$_{32}$ (configuration with Cr substitute Mn), $E(\text{Li}_8\text{CrNi}_4\text{Mn}_{11}\text{O}_{32})$ is the total energy of Li$_8$CrNi$_4$Mn$_{11}$O$_{32}$ (configuration with Cr substitute Mn), $E(\text{Li}_8\text{Ni}_4\text{Mn}_{12}\text{O}_{32})$ is the total energy of Li$_8$Ni$_4$Mn$_{12}$O$_{32}$. Chemical potentials of Cr, Ni, and Mn are the energy of per atom in metallic Cr, Ni, and Mn respectively.

For both of the undoped and Cr-doped LiNi$_{0.5}$Mn$_{1.5}$O$_4$, the stable configuration in each content of delithiation is constructed after fully considering all possible combinations. In more detail, There are $C^x_8$ kinds of combinations for $x$ Li ions extracting from the supercell, and the configurations with lowest energy in each delithiation states are used in the following computations.

The detail calculations for Convex Hull

The formation energies of intermediate phases Li$_{1-x}$Host are defined as:

$$\Delta E = E(\text{Li}_{1-x}\text{Host}) - (1-x) E(\text{LiHost}) - x E(\text{Host})$$

where $E(\text{Li}_{1-x}\text{Host})$ is the total energy per formula unit of the Li$_{1-x}$Host, $E(\text{LiHost})$ is the total energy per formula unit of the LiHost (fully lithiated configuration), and
$E(\text{Host})$ is the total energy per formula unit of the Host (fully delithiated configuration).

The Li vacancy formation energies of intermediate phases are defined as:

$$E_{\text{vac}} = E(\text{Li}_{1-x}\text{Host}) + E(\text{Li}) - E(\text{Li}_{1-(x-0.125)}\text{Host})$$

where $E(\text{Li}_{1-x}\text{Host})$ is the total energy of $\text{Li}_{1-x}\text{Host}$, $E(\text{Li})$ is the energy of an isolated Li atom, $E(\text{Li}_{1-(x-0.125)}\text{Host})$ is the total energy of $\text{Li}_{1-(x-0.125)}\text{Host}$ (the configuration contains one more Li atom comparing with $\text{Li}_{1-x}\text{Host}$).
**Supporting Figures**

**Fig S1.** Most stable configurations of (a) $\text{Cr}_{\text{Ni}}^-P$-$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (b) $\text{Cr}_{\text{Ni}}^-F$-$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (c) $\text{Cr}_{\text{Mn}}^-P$-$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and $\text{Cr}_{\text{Mn}}^-F$-$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

**Fig S2.** Formation energy and convex hulls of (a) $F$-$\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and (b) $\text{Cr}_{\text{Ni}}^-F$-$\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ as a function of delithiation content $x$. 
**Fig S3.** Illustration of 16 Li ion diffuse paths (a) and their corresponding (b) energy barriers in $F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$. Illustration of all 16 Li ion diffuse paths (c) and their corresponding (d) energy barriers in Cr$_{Ni}$-F-LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

**Fig S4.** Bond lengths and bond angles of TM rings in (a) $F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and (b) Cr$_{Ni}$-F-LiNi$_{0.5}$Mn$_{1.5}$O$_4$. 
Supporting Tables

**Table S1.** The relative energy difference between $P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and $F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

<table>
<thead>
<tr>
<th>Configurations</th>
<th>Relative energy difference (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$-LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>0.00</td>
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<tr>
<td>$F$-LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>0.71</td>
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</table>

**Table S2.** The defect formation energy of Cr$_{Ni}^{-}$-$P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Cr$_{Ni}^{-}$-$F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Cr$_{Mn}^{-}$-$P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and Cr$_{Mn}^{-}$-$F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

<table>
<thead>
<tr>
<th>Configurations</th>
<th>The defect formation energy (eV)</th>
</tr>
</thead>
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<tr>
<td>Cr$<em>{Ni}^{-}$-$P$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
<td>-3.60</td>
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<tr>
<td>Cr$<em>{Ni}^{-}$-$F$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
<td>-4.66</td>
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<td>Cr$<em>{Mn}^{-}$-$P$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
<td>-1.78</td>
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<tr>
<td>Cr$<em>{Mn}^{-}$-$F$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
<td>-2.13</td>
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**Table S3.** The total energy of Cr$_{Ni}^{-}$-$P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Cr$_{Ni}^{-}$-$F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, Cr$_{Mn}^{-}$-$P$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$, and Cr$_{Mn}^{-}$-$F$-LiNi$_{0.5}$Mn$_{1.5}$O$_4$.

<table>
<thead>
<tr>
<th>Configurations</th>
<th>Total energy (eV)</th>
</tr>
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<td>Cr$<em>{Ni}^{-}$-$P$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
<td>-361.95</td>
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<tr>
<td>Cr$<em>{Ni}^{-}$-$F$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
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<tr>
<td>Cr$<em>{Mn}^{-}$-$P$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
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<tr>
<td>Cr$<em>{Mn}^{-}$-$F$-LiNi$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
<td>-356.66</td>
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