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_{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*-$LiNi_{0.5}Mn_{1.5}O_4$ are shown in Fig S1.

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

$E_{def} = E(Li_8CrNi_3Mn_{12}O_{32}) - E(Li_8Ni_4Mn_{12}O_{32}) - \mu(Cr) + \mu(Ni)$

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

$E_{def} = E(Li_8CrNi_4Mn_{11}O_{32}) - E(Li_8Ni_4Mn_{12}O_{32}) - \mu(Cr) + \mu(Mn)$

where $E(Li_8CrNi_3Mn_{12}O_{32})$ is the total energy of $Li_8CrNi_3Mn_{12}O_{32}$ (configuration with Cr substitute Mn), $E(Li_8CrNi_4Mn_{11}O_{32})$ is the total energy of $Li_8CrNi_4Mn_{11}O_{32}$ (configuration with Cr substitute Mn), $E(Li_8Ni_4Mn_{12}O_{32})$ is the total energy of $Li_8Ni_4Mn_{12}O_{32}$. 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_8^x 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:

$\Delta E = E(Li_{1-x}Host) - (1-x)\,E(LiHost) - x\,E(Host)$

where $E(Li_{1-x}Host)$ is the total energy per formula unit of the $Li_{1-x}Host$, $E(LiHost)$ is the total energy per formula unit of the LiHost (fully lithiated configuration), and

E(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:

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

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

Supporting Figures

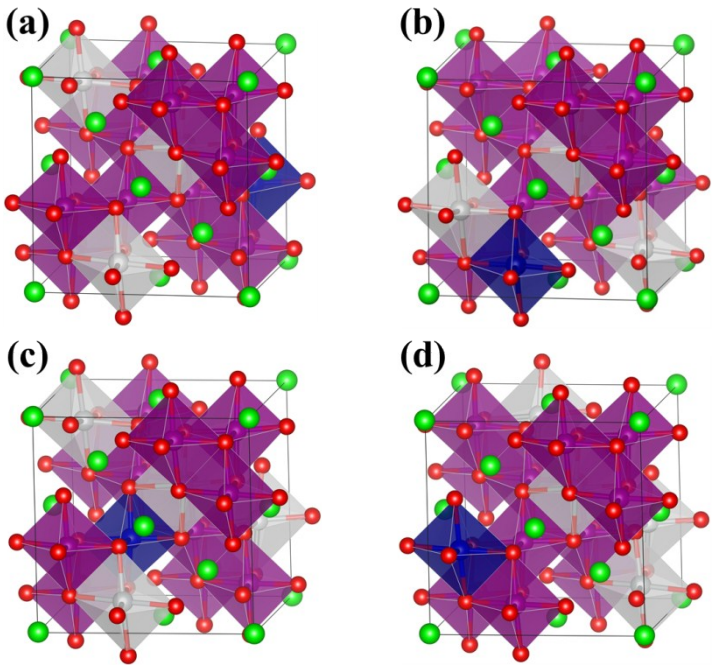

Fig S1. Most stable configurations of (a) Cr_{Ni}-*P*-$LiNi_{0.5}Mn_{1.5}O_4$, (b) Cr_{Ni}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$, (c) Cr_{Mn}-*P*-$LiNi_{0.5}Mn_{1.5}O_4$, and Cr_{Mn}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$.

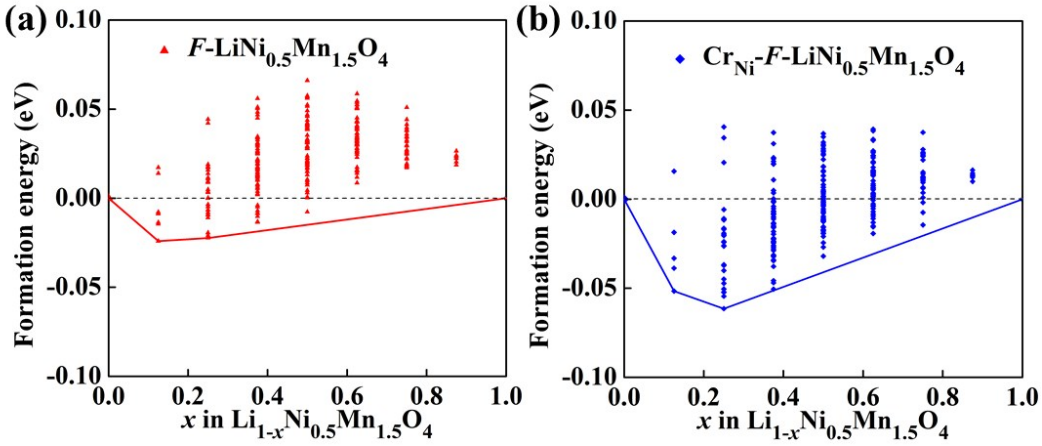

Fig S2. Formation energy and convex hulls of (a) *F*-$Li_{1-x}Ni_{0.5}Mn_{1.5}O_4$ and (b) Cr_{Ni}-*F*-$Li_{1-x}Ni_{0.5}Mn_{1.5}O_4$ as a function of delithiation content *x*.

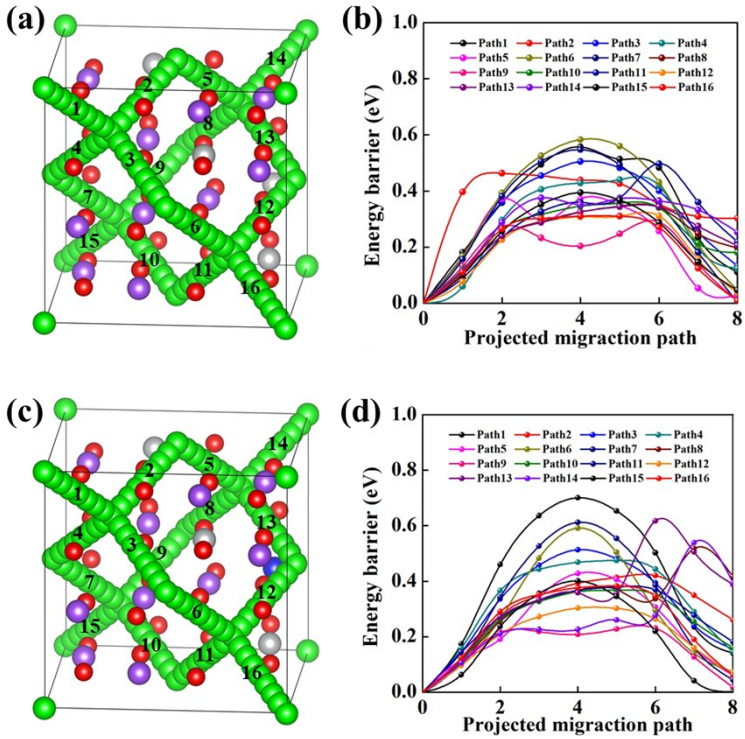

Fig S3. Illustration of 16 Li ion diffuse paths (a) and their corresponding (b) energy barriers in *F*-$LiNi_{0.5}Mn_{1.5}O_4$. Illustration of all 16 Li ion diffuse paths (c) and their corresponding (d) energy barriers in Cr_{Ni}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$.

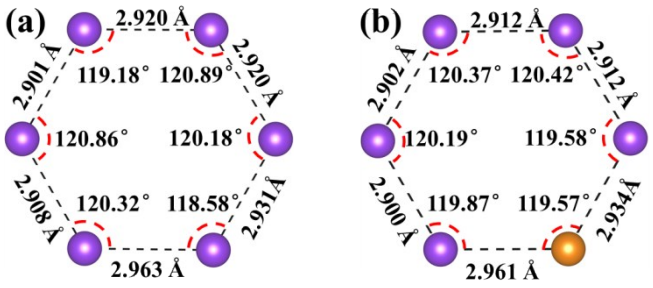

Fig S4. Bond lengths and bond angles of TM rings in (a) *F*-$LiNi_{0.5}Mn_{1.5}O_4$ and (b) Cr_{Ni}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$.

Supporting Tables

Table S1. The relative energy difference between *P*-$LiNi_{0.5}Mn_{1.5}O_4$ and *F*-$LiNi_{0.5}Mn_{1.5}O_4$.

Configurations	Relative energy difference (eV)
P-$LiNi_{0.5}Mn_{1.5}O_4$	0.00
F-$LiNi_{0.5}Mn_{1.5}O_4$	0.71

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*-$LiNi_{0.5}Mn_{1.5}O_4$.

Configurations	The defect formation energy (eV)
Cr_{Ni}-*P*-$LiNi_{0.5}Mn_{1.5}O_4$	-3.60
Cr_{Ni}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$	-4.66
Cr_{Mn}-*P*-$LiNi_{0.5}Mn_{1.5}O_4$	-1.78
Cr_{Mn}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$	-2.13

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*-$LiNi_{0.5}Mn_{1.5}O_4$.

Configurations	Total energy (eV)
Cr_{Ni}-*P*-$LiNi_{0.5}Mn_{1.5}O_4$	-361.95
Cr_{Ni}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$	-362.31
Cr_{Mn}-*P*-$LiNi_{0.5}Mn_{1.5}O_4$	-356.31
Cr_{Mn}-*F*-$LiNi_{0.5}Mn_{1.5}O_4$	-356.66