Electronic Supplementary Information

An interactive design for sustainable oxygen capacity in alkali-ion batteries

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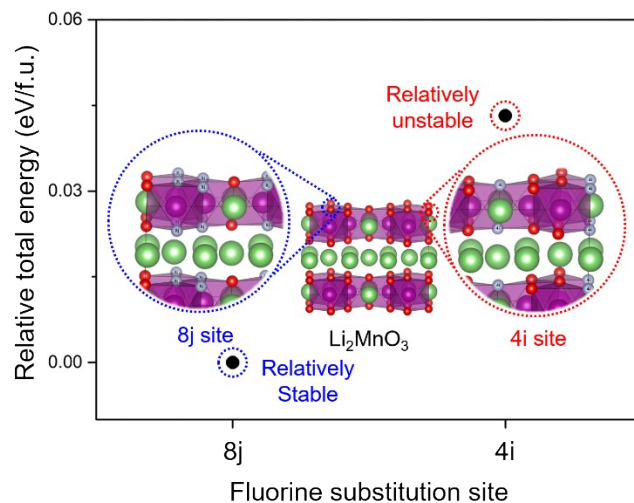E-mail: duhokim@khu.ac.kr (Prof. D. Kim).

Figure S1. Relative total energy depending on the two-type anionic sites in Li_2MnO_3. The anionic sites in the Li-excess Mn oxide can be broken down into 4i and 8j sites with respect to the Wyckoff positions. The energy diagram indicates that the F anion at the 8j site is relatively stable than that at the 4i site.
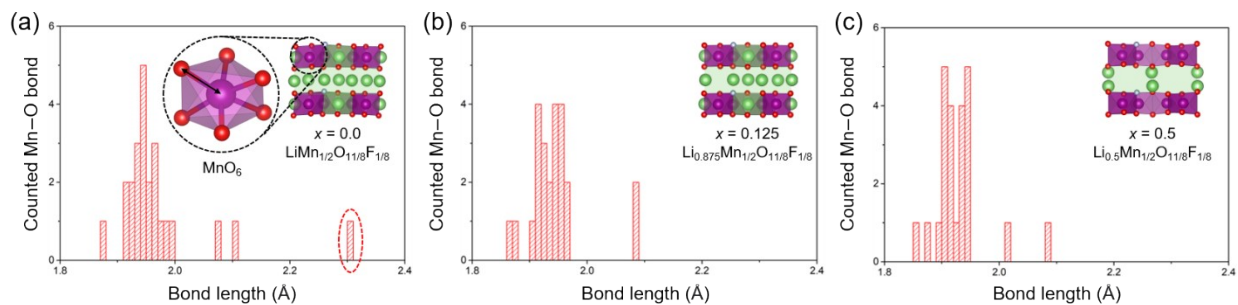
Figure S2. (a-c) Counted Mn−O bond length as a function of bond length from 1.8 to 2.4 Å depending on the ground states when the vacancy content is 0.0, 0.125, and 0.5, respectively. For better understanding, the atomic configurations of each ground state and six Mn−O bonds in MnO_6 are shown in the insets.
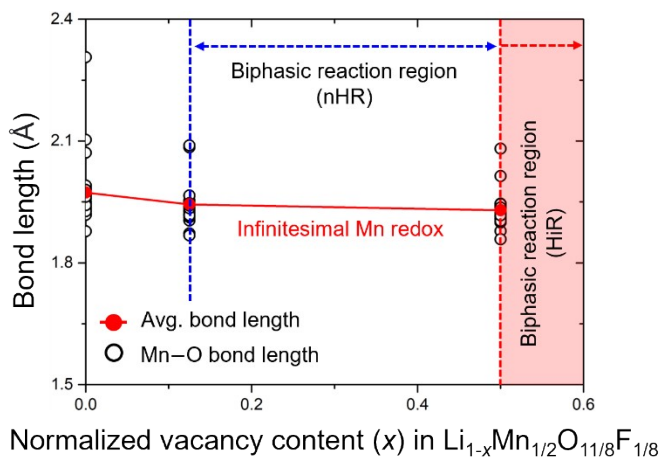
Figure S3. Computed Mn−O bond lengths (vacant black circle) and their averaged values (red-filled circle) in MnO_6 octahedrons from the pristine state ($x = 0.0$) to the first biphasic reaction region ($0.125 \leq x \leq 0.5$) in $Li_{1-x}Mn_{1/2}O_{11/8}F_{1/8}$.

Discussions of Figures S2-3

TM−O (TM denotes transition metals) bond usually decreases following the cationic redox during (de)intercalation in cathodes.[1,2] During the early stage of delithiation in $Li_{1-x}Mn_{1/2}O_{11/8}F_{1/8}$, the long Mn−O bond (~2.3 Å) disappears (red circle) when $0.0 \leq x \leq 0.125$, whereas the bond populations when $x = 0.125$ and 0.5 show the similar Mn−O bond population. For this reason, we can surmise that Mn redox does not dominantly take place after $x = 0.125$. Average Mn−O bond variation clearly shows the infinitesimal change when $0.125 \leq x \leq 0.5$ compared with that when $0.0 \leq x \leq 0.125$. The result also concurs with the expectation of triggering a single cationic redox reaction of Mn^{3+}/Mn^{4+} at the initial state of (de)intercalation and dominant participation of oxygen redox after $x = 0.125$.
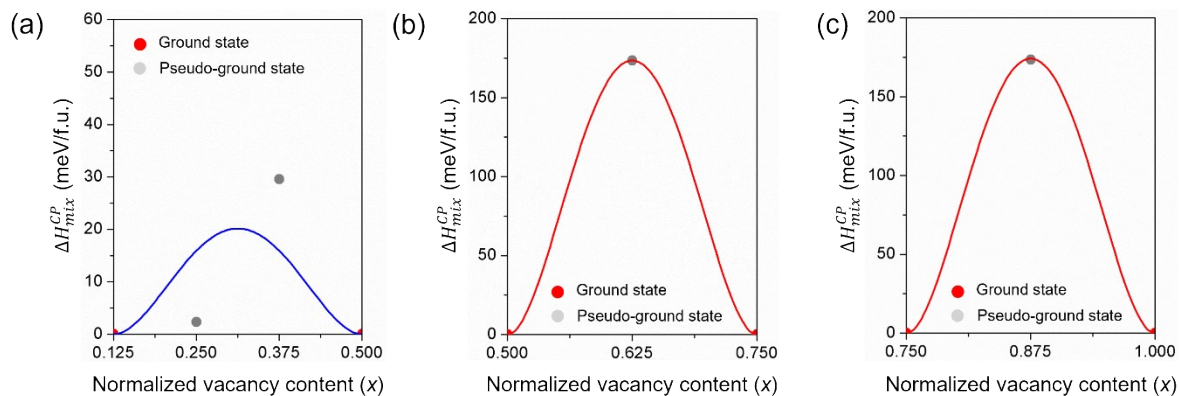
Figure S4. Combined phase mixing enthalpies fitted using the ground and pseudo-ground states that were determined by the convex hull diagram in Figure 1a, and their values were obtained based on the well-developed quadratic double-well model for (a) $0.125 \leq x \leq 0.5$, (b) $0.5 \leq x \leq 0.75$, and (c) $0.75 \leq x \leq 1.0$ in $Li_{1-x}Mn_{1/2}O_{11/8}F_{1/8}$.
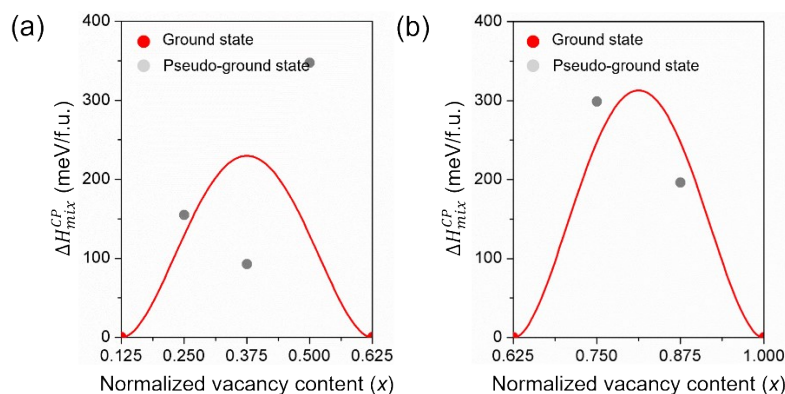
Figure S5. Combined phase mixing enthalpies fitted using the ground and pseudo-ground states that were determined by the convex hull diagram in Figure 2a, and their values were obtained based on the well-developed quadratic double-well model for (a) $0.125 \leq x \leq 0.625$, (b) $0.625 \leq x \leq 1.0$ in $Li_{1-x}Mn_{1/2}O_{11/8}F_{1/8}$. The height in the first region was much higher than that in the first biphasic region; therefore, it triggered serious hysteretic and irreversible (HiR) oxygen capacities upon (dis)charging. Also, that in the second region was considered HiR anionic capacity, even though its height was higher than that in the first region.

References

1   G. Choi, S. Park, S. Koo, J. Lee, D. Kwon and D. Kim, *ACS Appl. Mater. Interfaces*, 2021,

13, 46620–46626.

2   G. Choi, J. Lee, S. Koo, S. Park and D. Kim, *Cell Reports Phys. Sci.*, 2021, **2**, 100508.