ADDITIONAL INFORMATION

Supplementary information

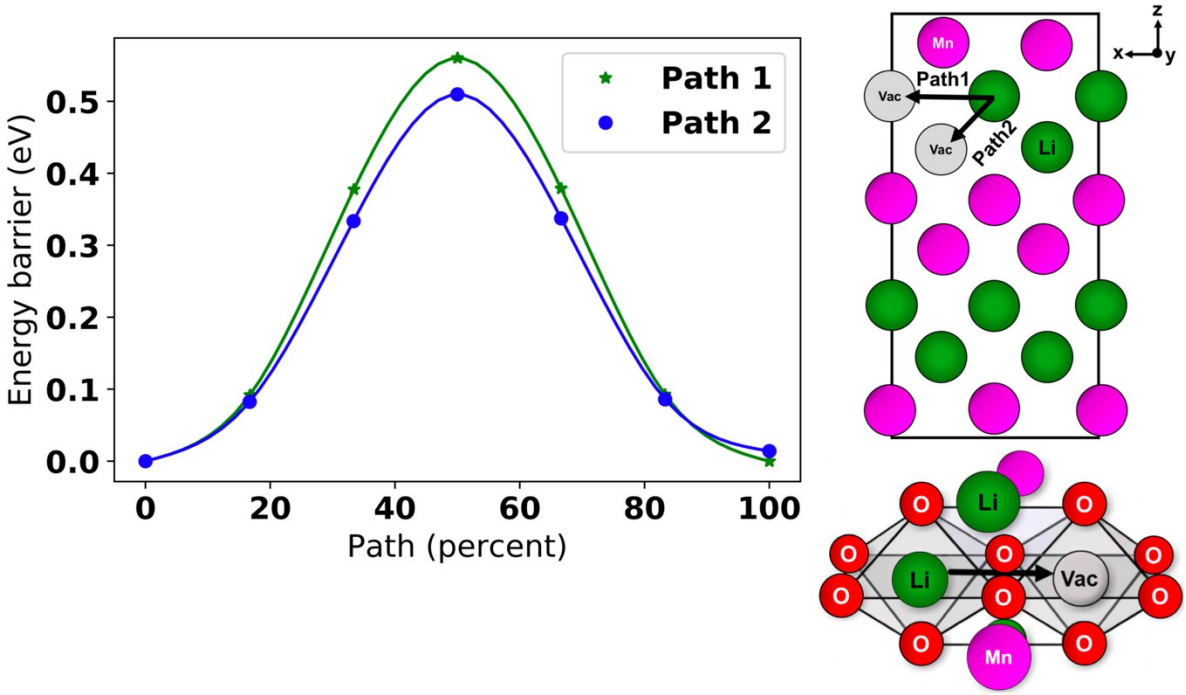

Figure S1: (left) Energy (eV) along the two possible paths (%) for a single vacancy mechanism in o-$LiMnO_2$. The in-plane hop (path 1) is shown in green with stars, and the out-of-plane hop (path 2) is shown in blue with filled circles. (bottom right) Magnified depiction showing the nearest neighbor cations along both paths. (top right) Atomic configuration demonstrating the Li hops, which occur along the trajectory shown by the black arrow along the (010) plane.

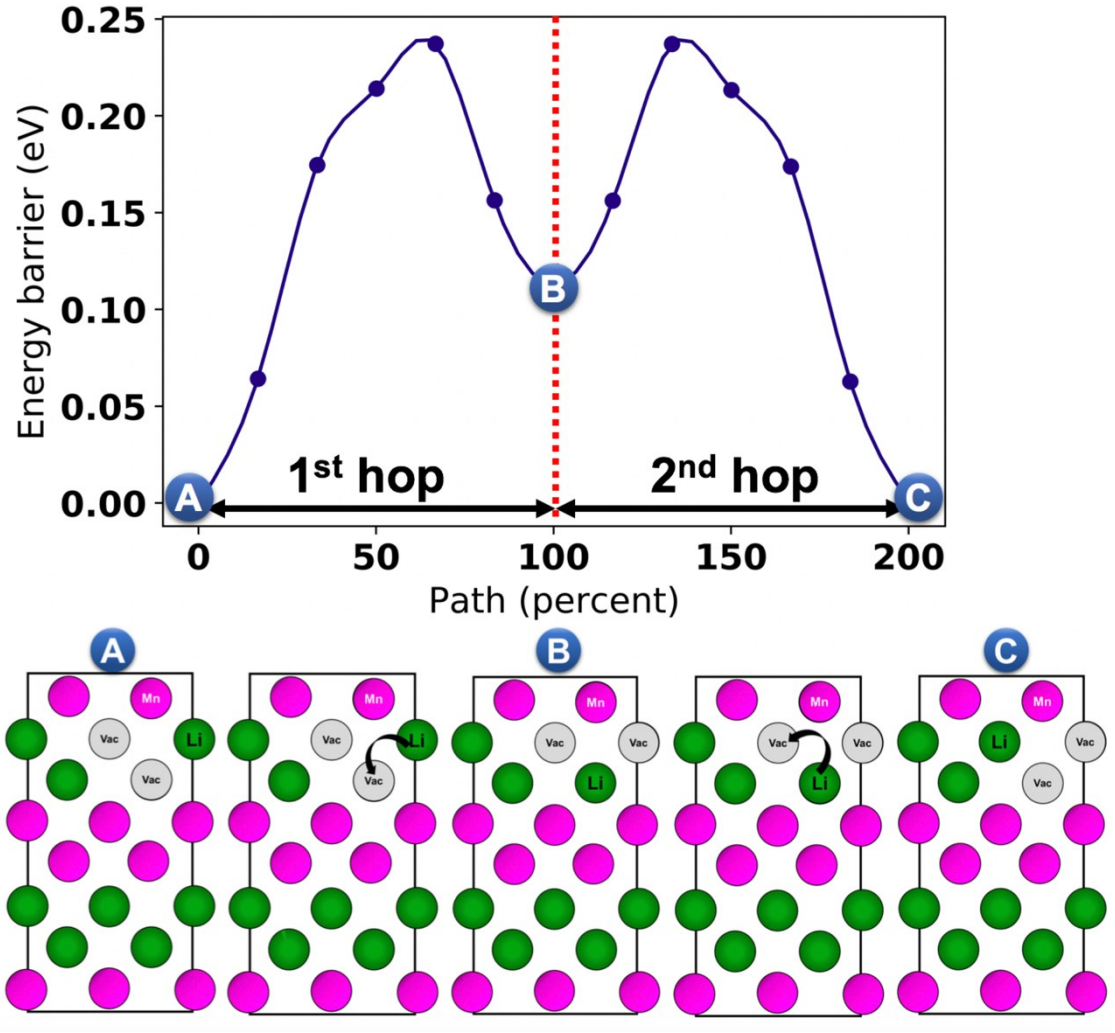

Figure S2: (top) Energy (eV) along Li migration path (%) consisting of two separate hops that constitute a full percolating path using the divacancy migration mechanism in o-$LiMnO_2$. (bottom) Atomic configurations of the hops before, during, and after the hops. Green, purple, and gray circles represent Li, Mn, and vacancies. O atoms are not shown for clarity. Position A in both top and bottom figures correspond to the case when two vacancies are not in the same plane but share an edge, while position B corresponds to the case when the vacancies are in the same plane. Position C is symmetrically equivalent to position A.

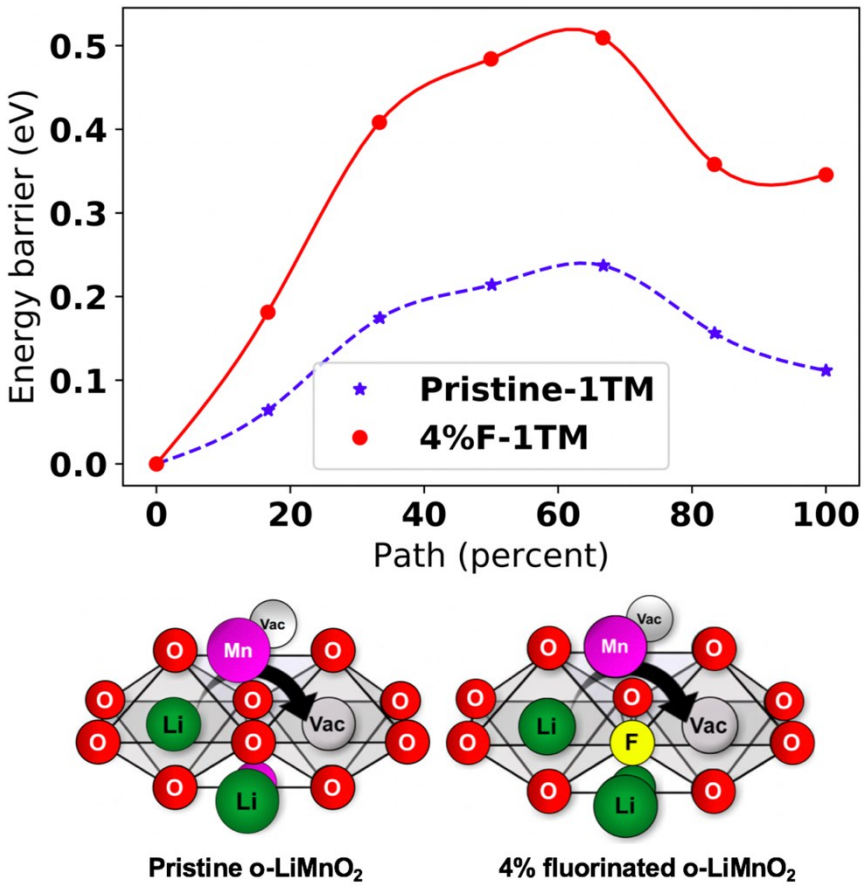

Figure S3: Energy (eV) along Li migration path (%) for 1-TM divacancy Li migration mechanism in pristine (dotted blue line) and 4% fluorinated o-$LiMnO_2$ (solid red line marked with filled circle). Atomic configurations are shown below the graph. Green, purple, red, yellow, and light gray show Li, Mn, O, F, and vacancy respectively.

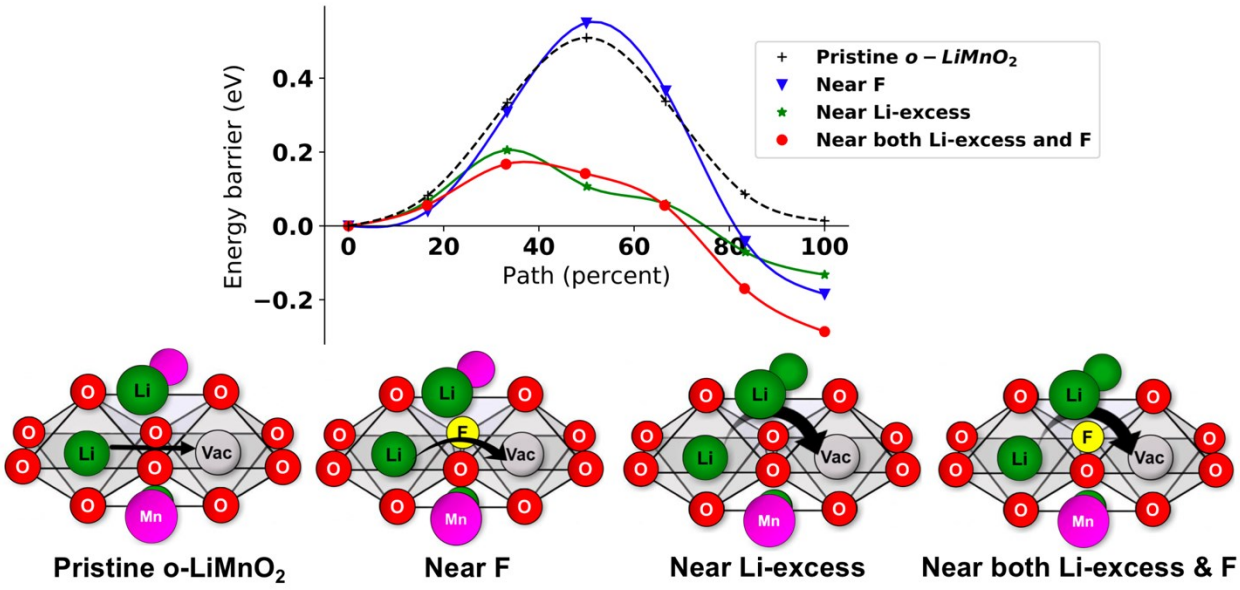

Figure S4: Energy (eV) along Li migration path (%) for single vacancy migration mechanism for cases when the migrating ion is in pristine o-$LiMnO_2$ (black dashed line, marked with plus sign), near F (solid blue curve, marked with triangle), near Li-excess (solid green curve, marked with star), and near both F and Li-excess (solid red color, marked with filled circle) from one octahedral site to another octahedral site. Atomic configurations are shown below the graph. Green, purple, red, yellow, and light gray show Li, Mn, O, F, and vacancy respectively. The black arrows on the atomic configurations correspond to the migration trajectory of the Li ion. Note that the o-$LiMnO_2$ has corrugated Li and Mn layers. Therefore, the initial and final sites of the migrating Li ion have different nearest neighbor cation environments in all cases except the pristine structure.

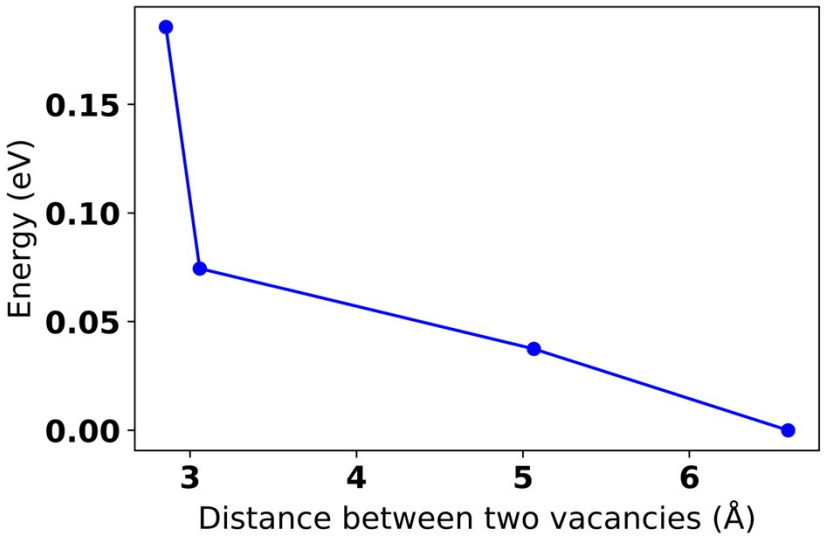

Figure S5: Energy (eV) of two vacancies separated at different distances. All the energies on the *y* axis are adjusted relative to the energy of the lowest energy configuration which here corresponds to a separation between two vacancies of 6.6 Å.

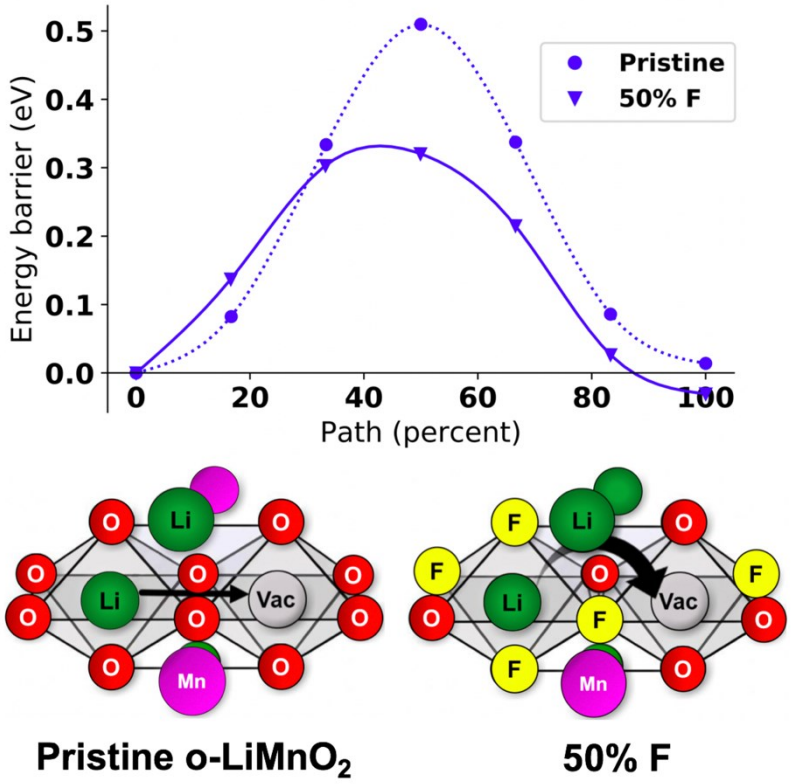

Figure S6: Energy (eV) along Li migration path (%) for 1-TM, out-of-plane hop (solid blue line) single vacancy Li migration mechanism in 50% fluorinated o-$LiMnO_2$. The MEP of the single vacancy migration mechanism for the pristine structure (dotted blue line) is replotted for the purpose of comparison. Atomic configurations are shown below the graph. Green, purple, red, yellow, and light gray show Li, Mn, O, F, and vacancy respectively.

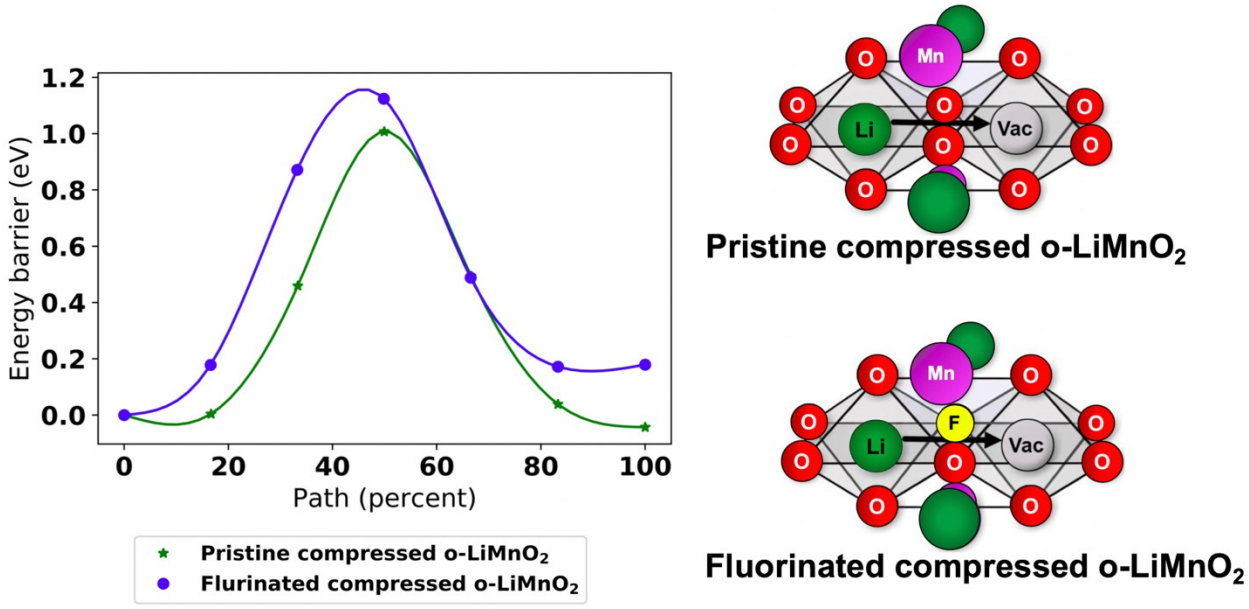

Figure S7: Energy (eV) along Li migration path (%) for 1-TM single vacancy Li migration mechanism in pristine and 3% fluorinated o-$LiMnO_2$ under compression. Atomic configurations are shown on the right. Green, purple, red, yellow, and light gray show Li, Mn, O, F, and vacancy respectively.

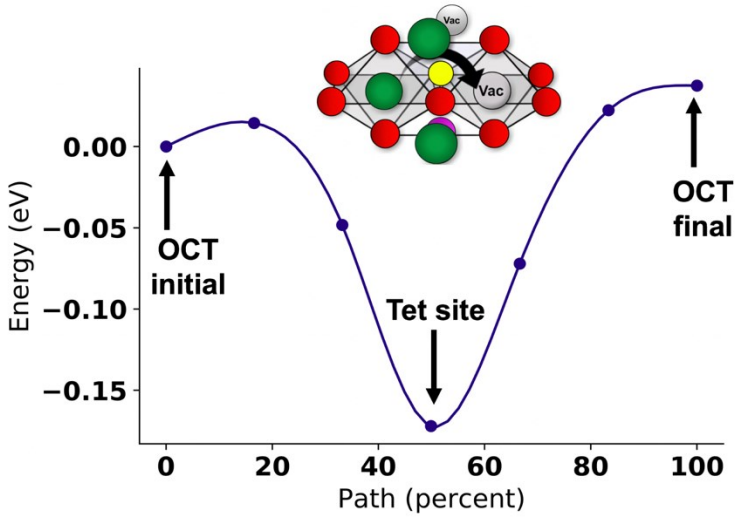

Figure S8: Energy landscapes along the migration path for 0-TM divacancy diffusion in a slightly fluorinated (4% F) o-$LiMnO_2$ structure. Also shown as an inset is the local atomic configurations with the Li trajectory shown by the black arrow in the atomic configurations, with black labels indicating the octahedral initial and final sites and tetrahedral intermediate sites. Li, Mn, O, F, and vacancy are depicted as green, purple, red, yellow, and light grey spheres.