Supporting information for insight into fast Li diffusion in Li-excess spinel lithium manganese oxide

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Case of lithium interstitial

We only considered the lithium antisites created by replacing some of the Mn ions in the 16d sites with Li ions in the manuscript. As we mentioned in the introduction part, lithium antisite is dominant among all possible ionic defects in $LiMn_2O_4$ according to previous works (*J. Mater. Chem. A*, 2014, **2**, 18271-18280), and the resulting Li-excess phases $Li_{1+x}Mn_{2-x}O_4$ are equilibrium phases (*Chem. Mater.*, 1999, **11**, 3065-3079). To further confirm this, we calculated lithium interstitial with the extra Li ion occupying the 16c site, which is shown in **Figure S1**.

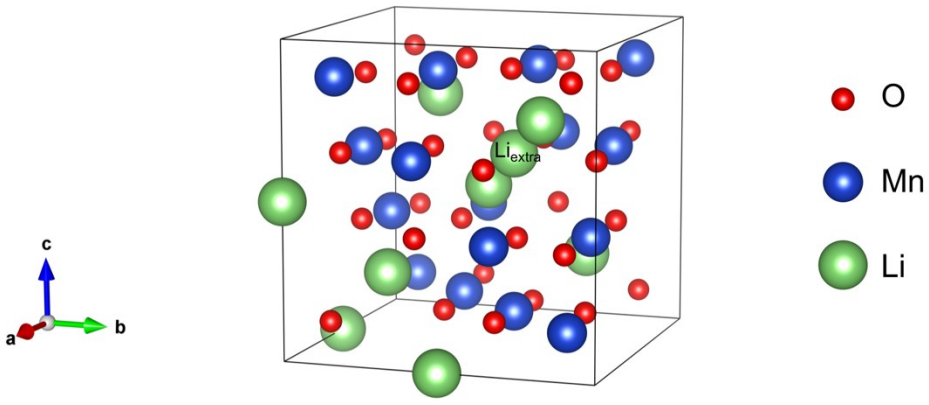

Figure S1. Crystal structure of spinel lithium manganese oxide with an extra Li ion in the interstitial 16c site.

Again, we were going to investigate the energy barrier of Li migration with Li ions at the interstitial sites using the cNEB method. As mentioned in the manuscript, the first step of

cNEB calculation is to calculate the initial and end point configurations. The location of the hopped Li ion and a vacancy were specified, and then the structures were optimized. **Figure S2** shows the results. After structure optimization, the extra Li ion in the interstitial site automatically fills in the adjacent Li vacancy, indicating that the lithium interstitial is very unstable. So there is neither feasibility nor necessity to continue the cNEB calculation, and considering the lithium antisites sounds enough.

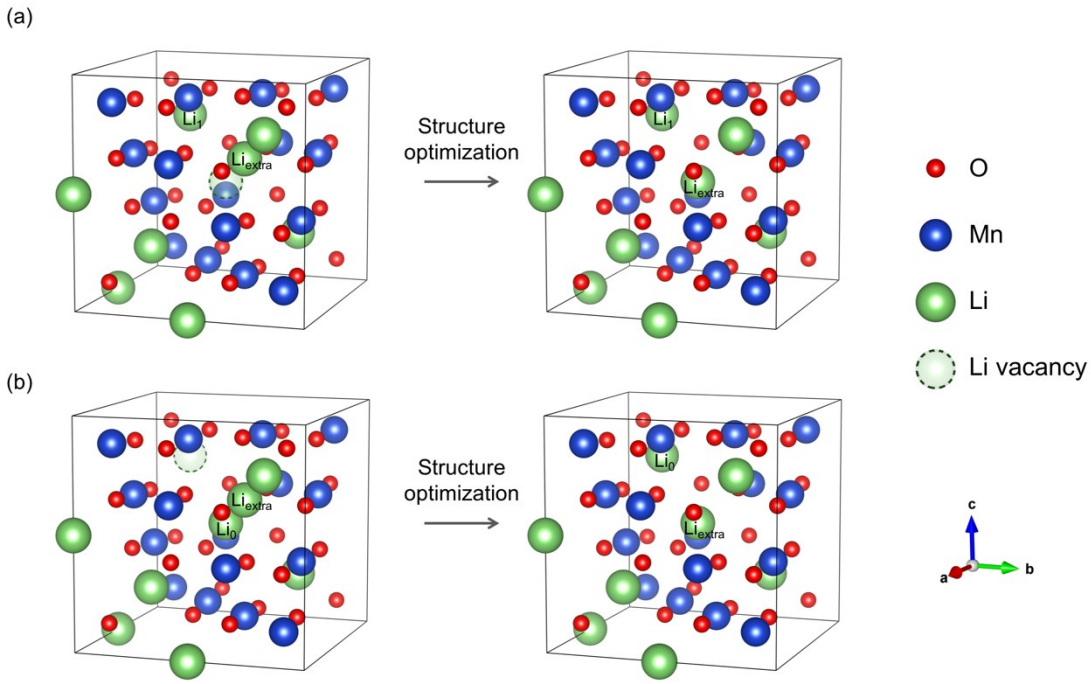

Figure S2. Ions locations before and after structure optimization of the initial (a) and end (b) configurations.