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Supplementary Materials for

Interplay of cation and anion redox in $Li_4Mn_2O_5$ cathode material and prediction of improved $Li_4(Mn,M)_2O_5$ electrodes for Li-ion batteries

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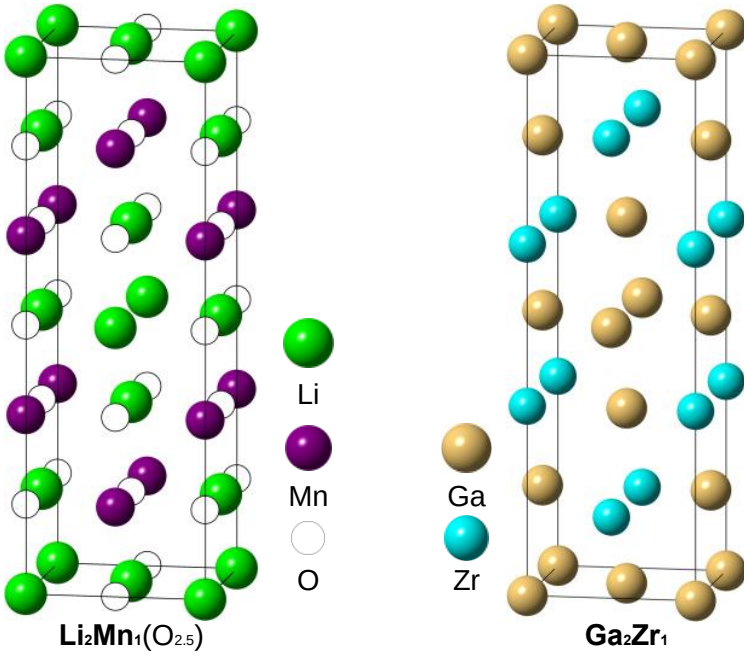

fig. S1. Cationic ordering between Li and Mn in $Li_4Mn_2O_5$ and between Ga and Zr in Ga_2Zr. The cationic ordering between $Li_4Mn_2O_5$ and Ga_2Zr is identical.

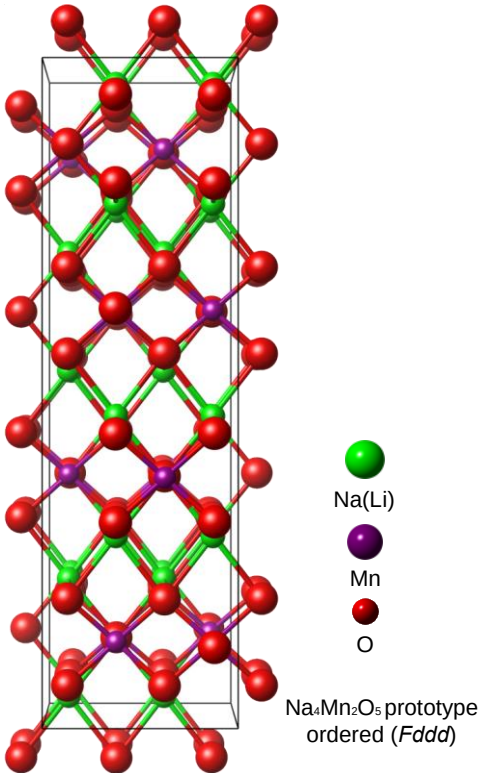

fig. S2. $Na_4Mn_2O_5$ prototype structure with a space group *Fddd*.

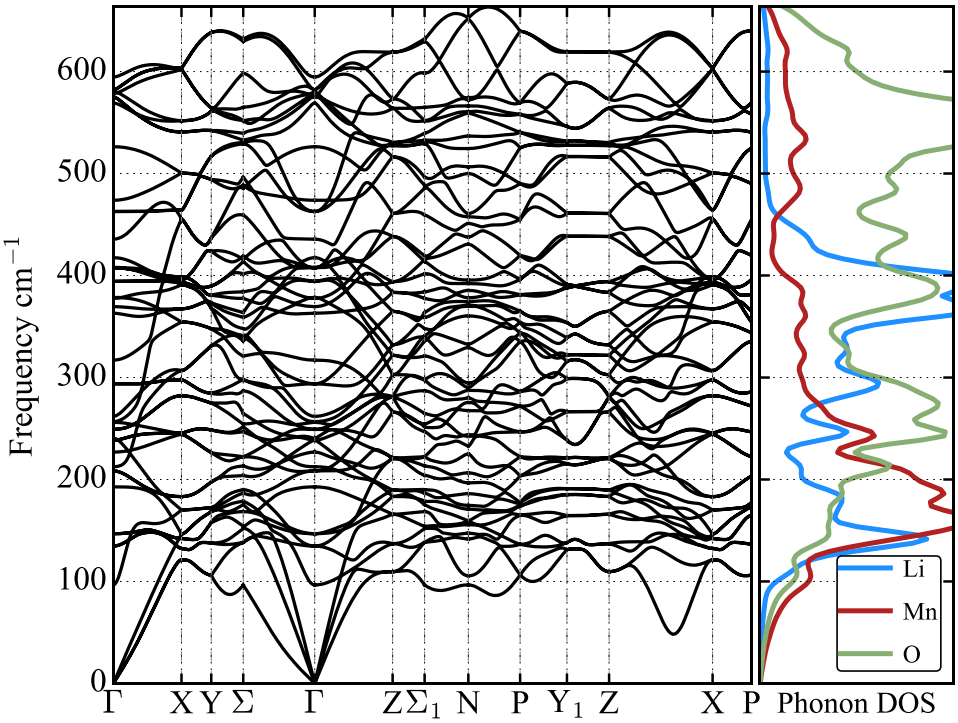

fig. S3. Phonon dispersion of the ground-state $LiMnO_2$.

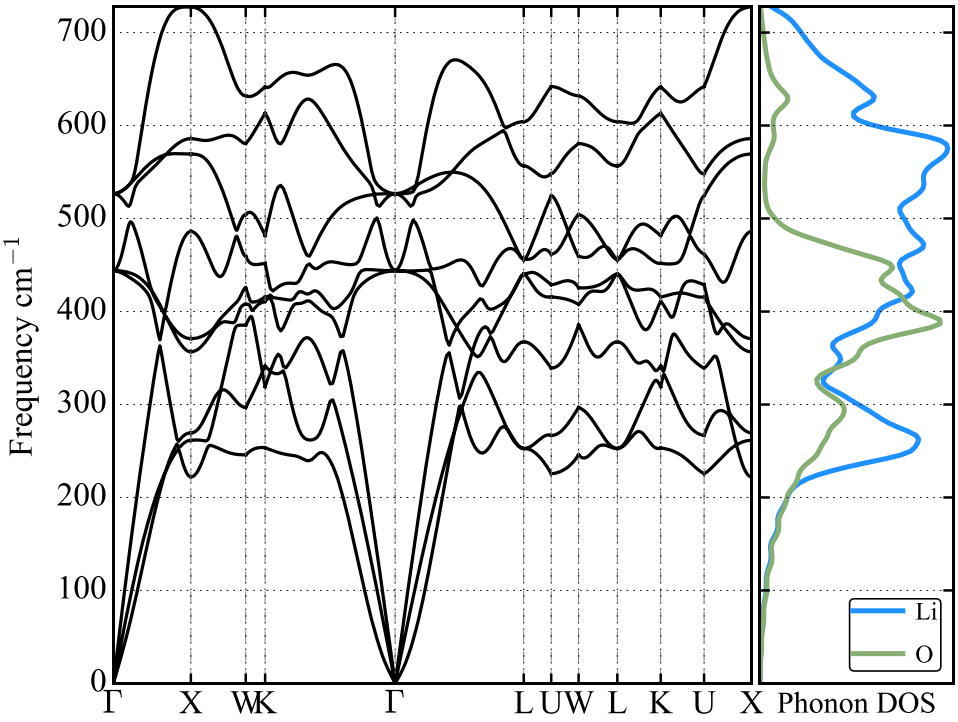

fig. S4. Phonon dispersion of the ground-state Li_2O.

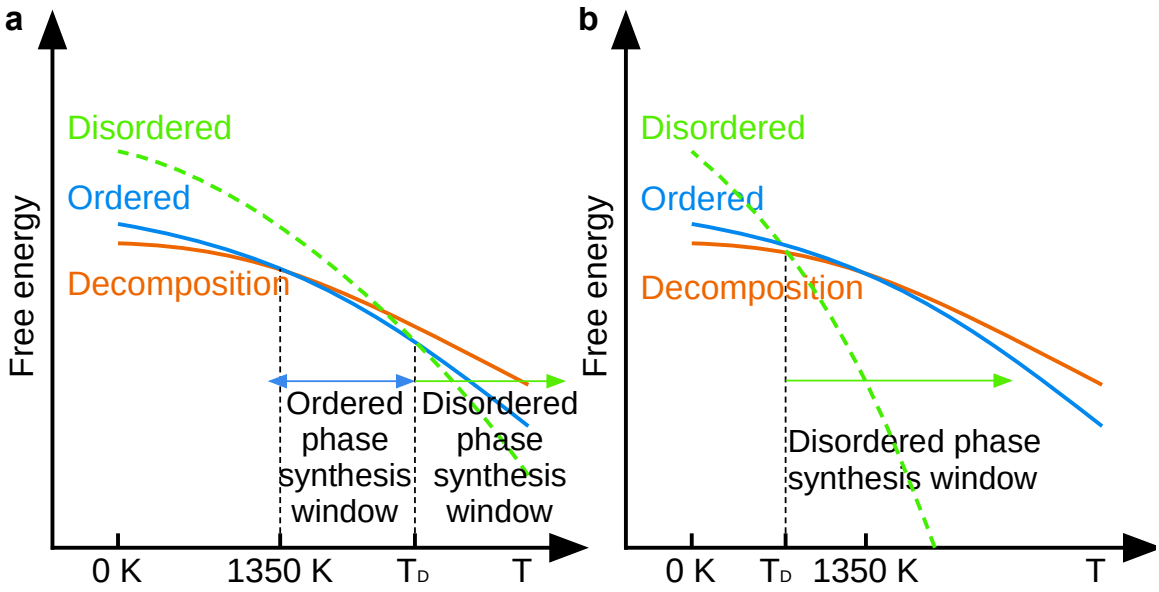

fig. S5. Schematic illustration of the relative stabilities between the disordered and ordered $Li_4Mn_2O_5$, as well as the decomposed combination, $2LiMnO_2 + Li_2O$. Temperature-dependent free energies for the disordered, ordered and decomposition combination are exhibited by green (dash), blue (solid), and orange (solid) lines, respectively.

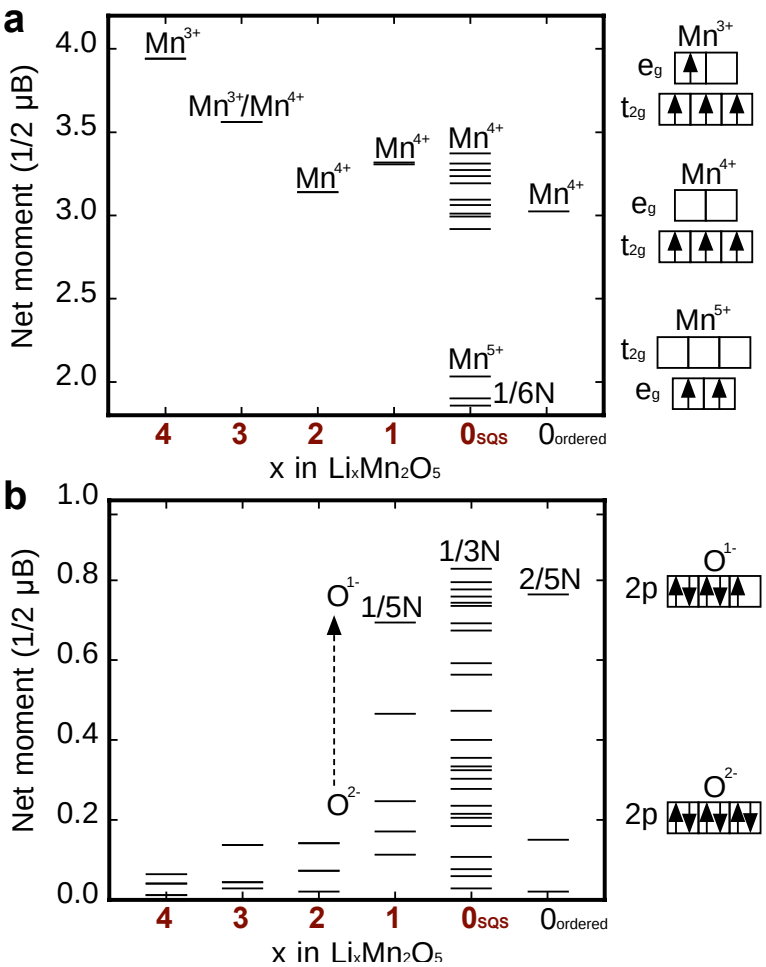

fig. S6. The magnetization and oxidation evolution of Mn and O ions during delithiation. The magnetization and oxidation state evolution of (**a**) Mn and (**b**) O ions in intermediate phases $Li_xMn_2O_5$ (x = 4, 3, 2, 1, and 0) during delithiation. In nearly-delithiated intermediated phases (x = 2, 1, 0_{SQS}, $0_{ordered}$), oxidation states of Mn and O ions are not identical with the partition of certain oxidation state marked by fractions (*i.e.* 1/5N). Mn and O magnetizations show wide distribution in the x = 0 phase as a result of the various local environments of Mn in the disordered SQS structure. The electronic configurations of Mn^{3+}, Mn^{4+}, Mn^{5+}, O^{2-}, and O^{1-} are presented. Mn and O magnetizations in ordered Mn_2O_5 shown as a reference.

table S1. Structure information of the $Li_4Mn_2O_5$ ground state. Space group name: Cmmm

Lattice parameters: a = 4.0390 Å, b = 12.4312 Å, c = 4.0268 Å, α = β = γ = 90.0000°

Structure parameters:

Atom	*x*	*y*	*z*	*occupancy*
Li1	0.0000	0.0000	0.0000	1
Li2	0.5000	0.5000	0.0000	1
Li3	0.0000	0.5000	0.5000	1
Li4	0.5000	0.0000	0.5000	1
Li5	0.0000	0.6847	0.0000	1
Li6	0.5000	0.1847	0.0000	1
Li7	0.5000	0.8153	0.0000	1
Li8	0.0000	0.3153	0.0000	1
Mn1	0.0000	0.1594	0.5000	1
Mn2	0.5000	0.6594	0.5000	1
Mn3	0.5000	0.3406	0.5000	1
Mn4	0.0000	0.8406	0.5000	1
O1	0.0000	0.0000	0.5000	1
O2	0.5000	0.5000	0.5000	1
O3	0.0000	0.6669	0.5000	1
O4	0.5000	0.1669	0.5000	1
O5	0.5000	0.8314	0.5000	1
O6	0.0000	0.3331	0.5000	1
O7	0.0000	0.1557	0.0000	1
O8	0.5000	0.6557	0.0000	1
O9	0.5000	0.3443	0.0000	1
O10	0.0000	0.8443	0.0000	1

table S2. Top $Li_4(Mn,M)_2O_5$ cathode candidates from the HT-DFT screening with predicted gravimetric capacities (theoretical) and averaged voltages using $Li_4Mn_2O_5$ as the benchmark.

Reactions	Capacity C_g ($mAh\ g^{-1}$)	Voltage E_{avg} (V)
$Li_4Mn_2O_5 \rightarrow 4Li^+ + 4e^- + Mn_2O_5$	492	3.75
$Li_4MnVO_5 \rightarrow 4Li^+ + 4e^- + MnVO_5$	502	3.10
$Li_4MnCrO_5 \rightarrow 4Li^+ + 4e^- + MnCrO_5$	499	3.69