Supporting Information

Unraveling the divalent pillar effects for the prolonged cycling of high-energy-density cathodes

Byungwook Kang,[†a] Hyungjun Kim,[†a] Myungkyu Kim [a], Duho Kim, [*b] and Maenghyo Cho [*a]

[a]*Department of Mechanical Engineering, Seoul National University, Gwanak-ro 1, Gwanak-gu, Seoul 08826, Republic of Korea*
[b]*Department of Mechanical Engineering (Integrated Engineering Program), Kyung Hee University, 1732, Deogyeong-daero, Giheung-gu, Yongin-si, Gyeonggi-do, 17104, Republic of Korea*
[†]These authors contributed equally.

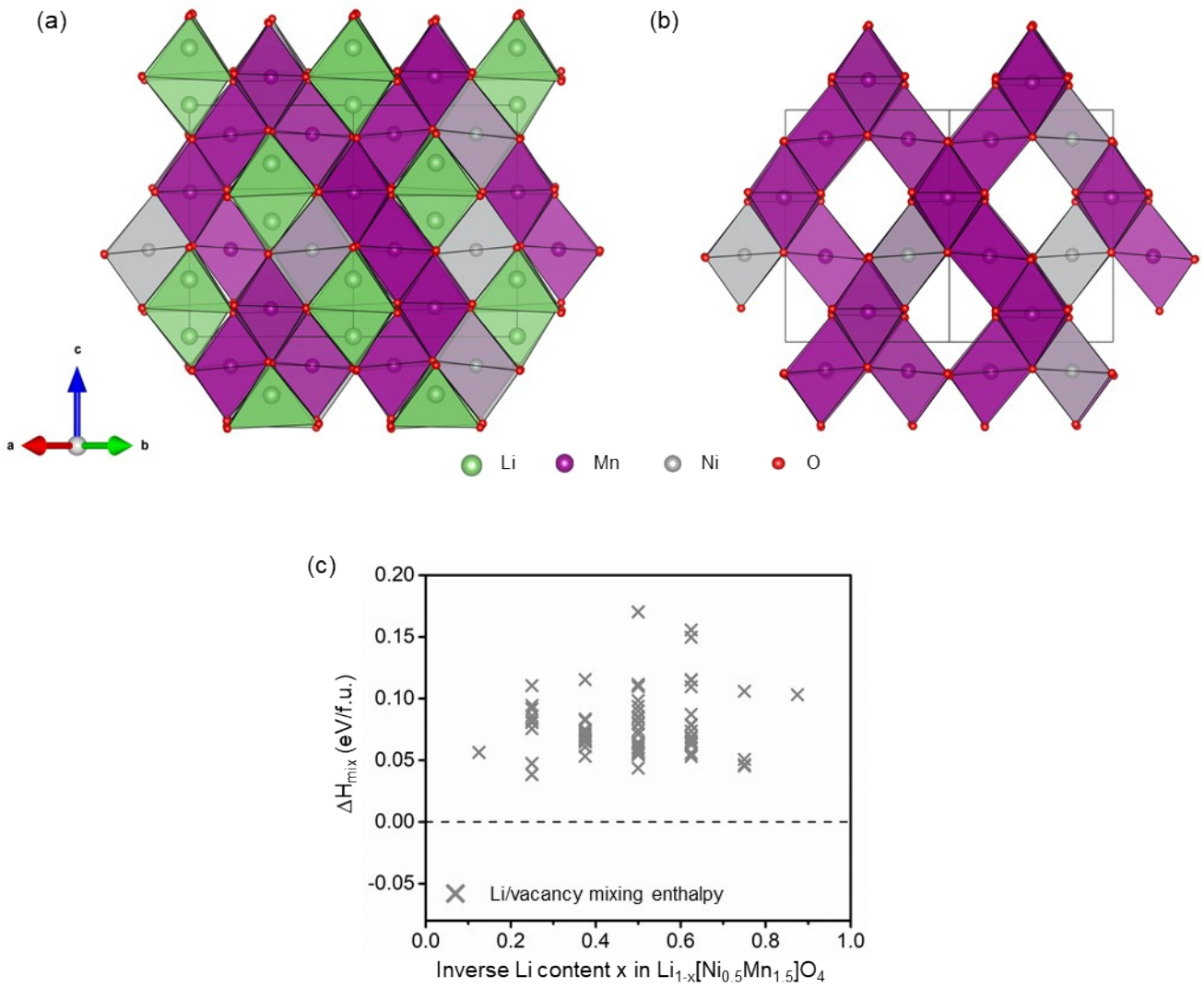

Figure S1. Atomic models of (a) fully lithiated LNMO and (b) fully delithiated LNMO projected onto the (110) plane. (c) Calculated mixing enthalpy energies of LNMO.

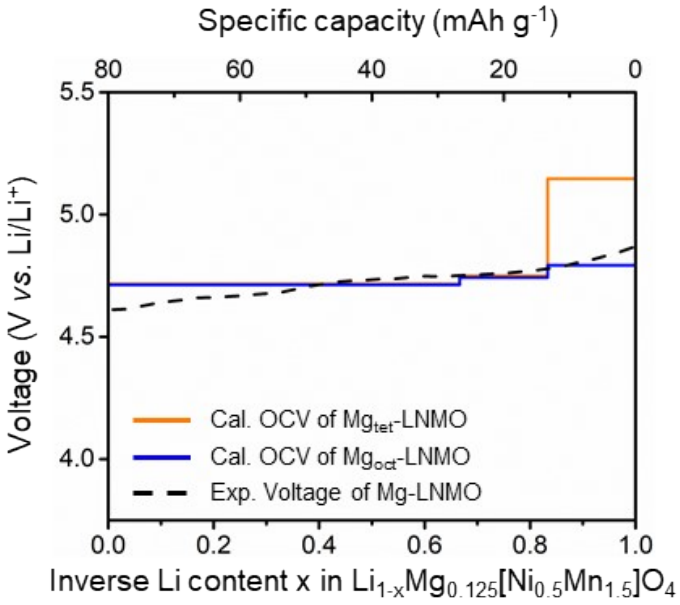

Figure S2. Calculated open-circuit voltage versus Li/Li^+ of Mg_{tet}-LNMO (orange, solid line), Mg_{oct}-LNMO (blue, solid line) from DFT, and voltages at the 100th cycle for Mg-LNMO (black, dashed line) reproduced from the experimental data of Liang *et al.*[23]

Table S1. Calculated Mg vacancy formation energies of Mgtet-LNMO (upper) and Mgoct-LNMO (lower) from DFT.

Material	Concentration	E_f [eV/f.u.]
Mg_{tet}-LNMO	x = 0	7.785
	x = 0.666	7.144
	x = 0.833	6.972
	x = 1	6.183
Mg_{oct}-LNMO	x = 0	7.097
	x = 0.666	7.310
	x = 0.833	6.682
	x = 1	6.247

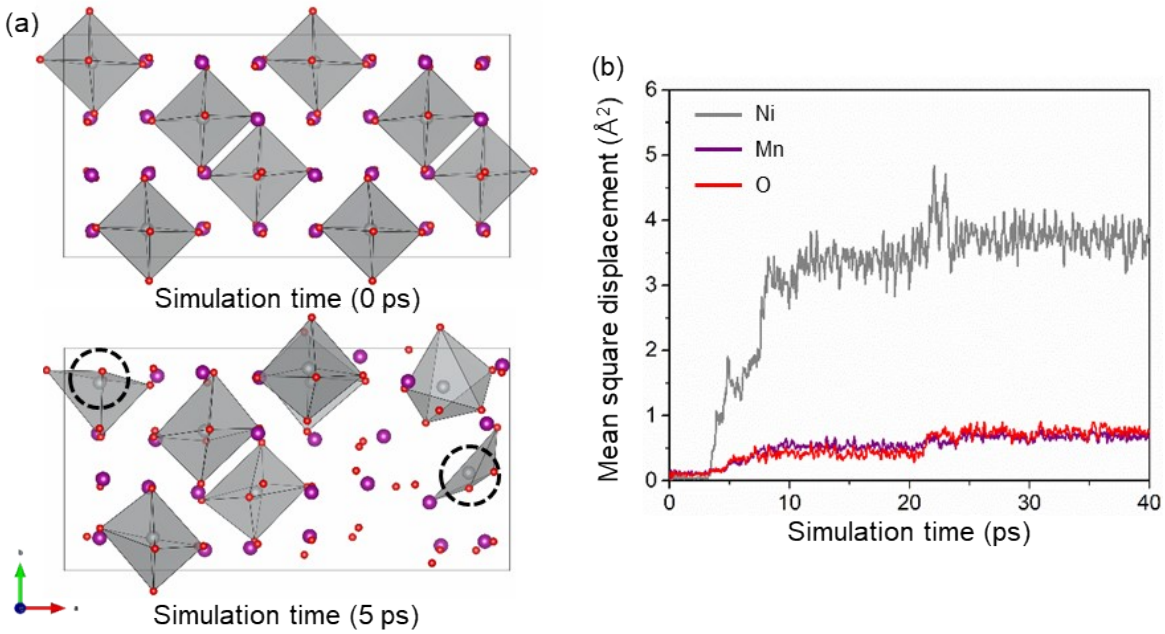

Figure S3. (a) Snapshots of the LNMO structure in the initial state (upper) and the state at which Ni ion migration begins at 600 K. (b) Mean square displacements of Ni (grey), Mn (purple), and O (red) ions at 600 K as functions of the simulation time.

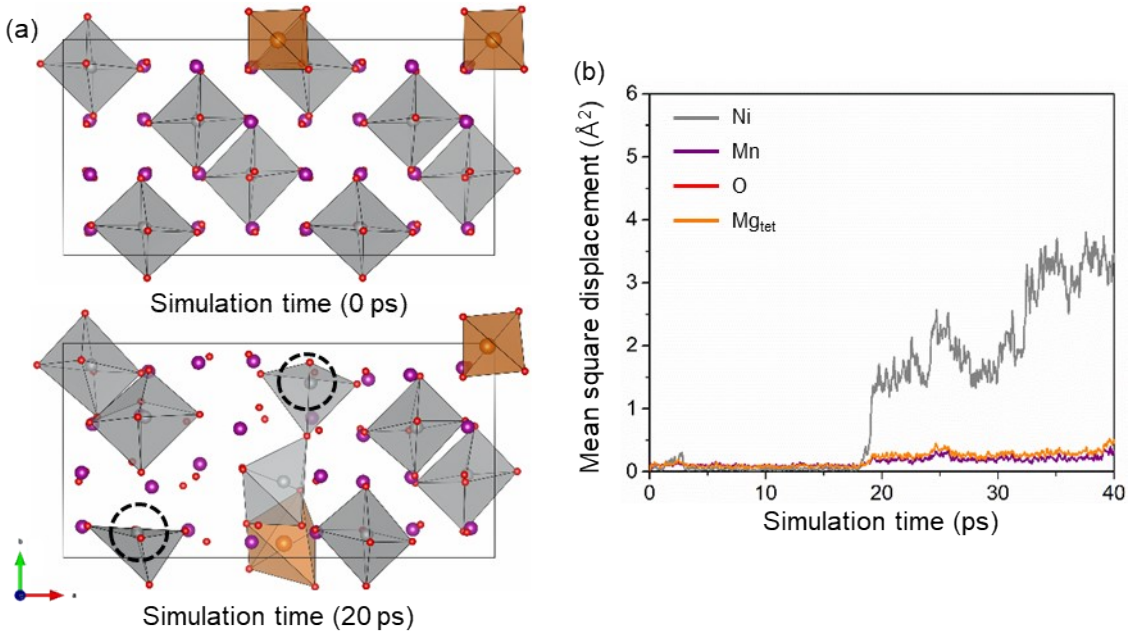

Figure S4. (a) Snapshots of the Mg_{tet}-LNMO structure in the initial state (upper) and the state at which Ni ion migration begins at 600 K. (b) Mean square displacements of Ni (grey), Mn (purple), O (red), and Mg_{tet} (orange) ions at 600 K as functions of the simulation time.

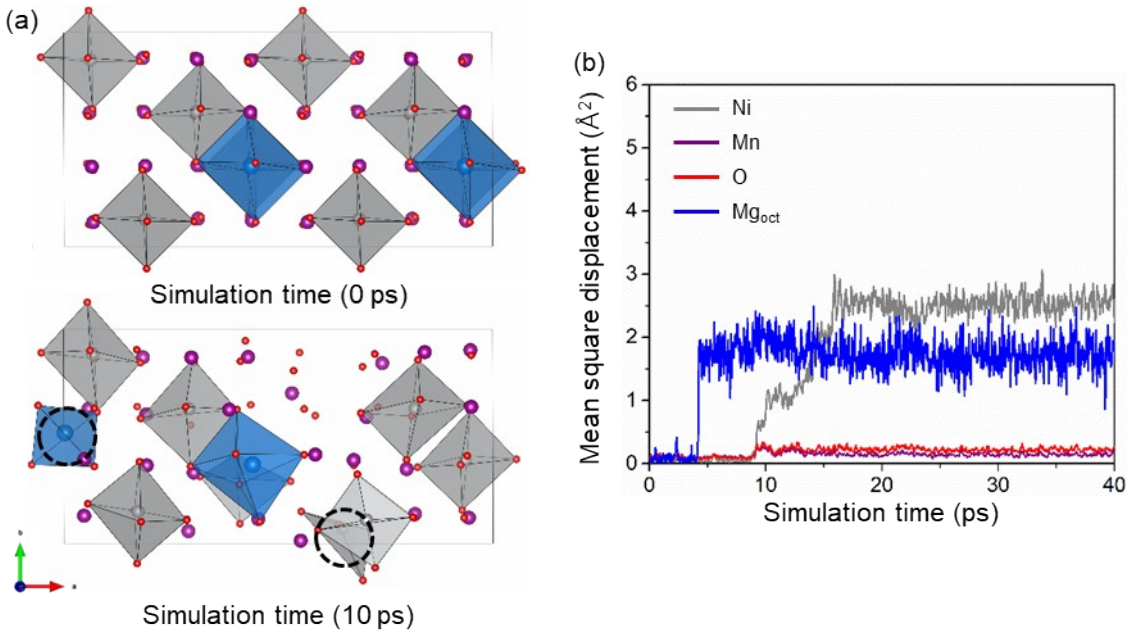

Figure S5. (a) Snapshots of the Mg_{oct}-LNMO structure in the initial state (upper) and state at which Ni ion migration begins at 600 K. (b) Mean square displacements of Ni (grey), Mn (purple), O (red), and Mg_{oct} (blue) ions at 600 K as functions of the simulation time.