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Supporting Information for

Underlying Mechanisms on Synergistic Role of Li_2MnO_3 and $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ in High-Mn, Li-rich Oxides

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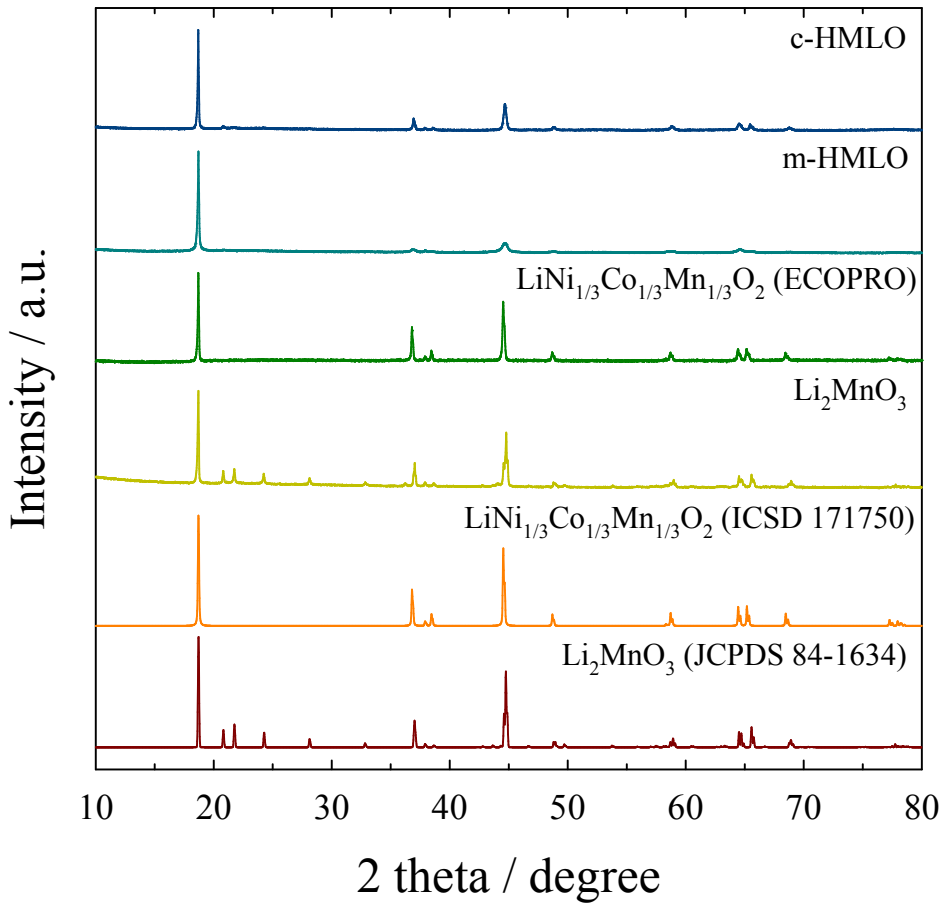

Figure S1. Powder XRD patterns of reference Li_2MnO_3 (JCPDS 84-1634), reference $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (ICSD 171750), as-synthesized Li_2MnO_3, commercialized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (ECOPRO), m-HMLO, and c-HMLO.

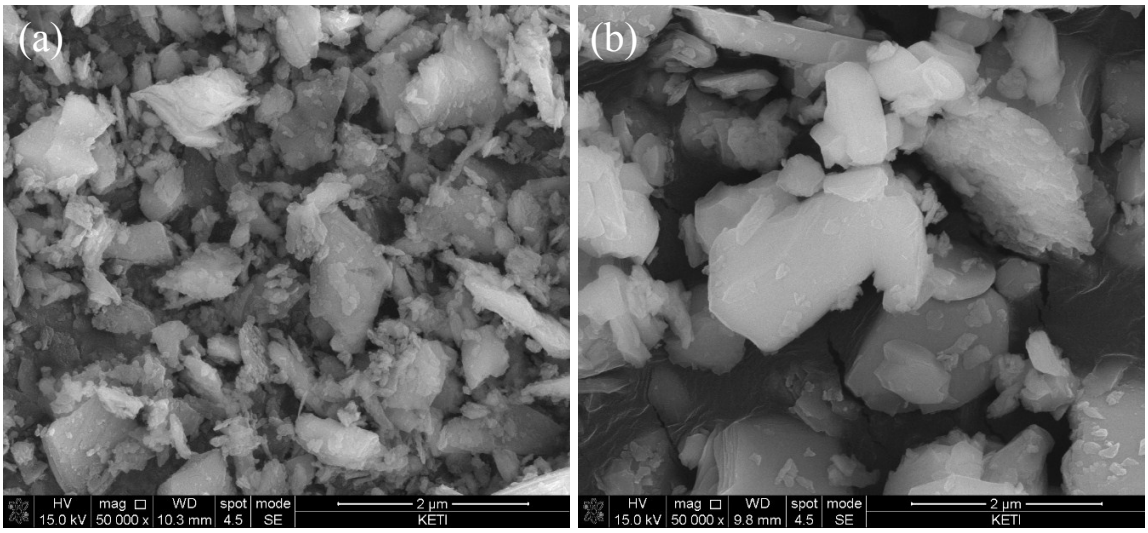

Figure S2. FESEM images of m-HMLO (a) and c-HMLO (b).

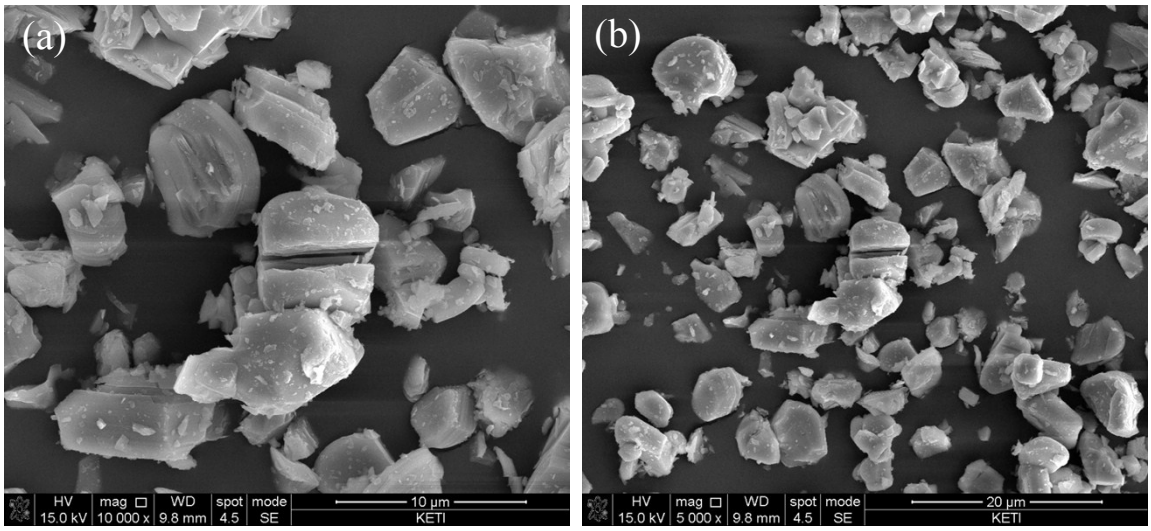

Figure S3. Field-emission scanning electron microscope (FESEM) images of as-synthesized Li_2MnO_3 at low magnification (a) and high magnification (b).

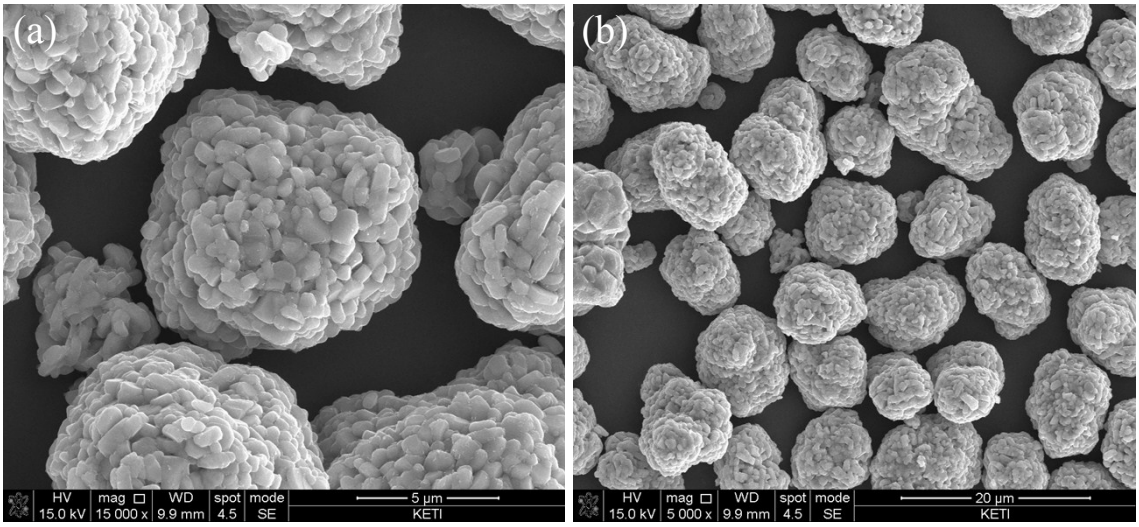

Figure S4. Field-emission scanning electron microscope (FESEM) images of commercialized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ at low magnification (a) and high magnification (b).

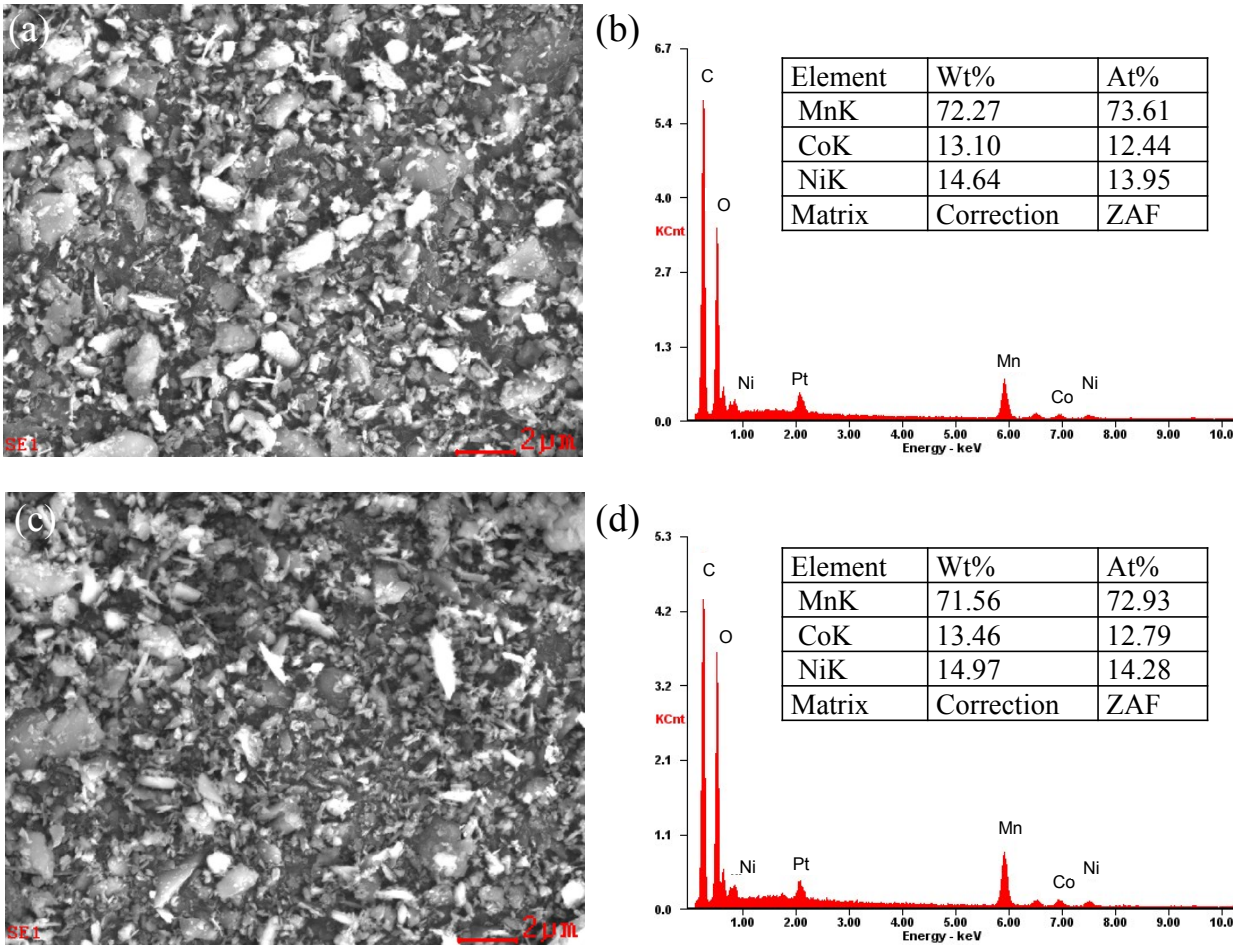

Figure S5. (a, c) FESEM images of m-HMLO at different two locations; (b, d) EDS patterns with the corresponding composition table.

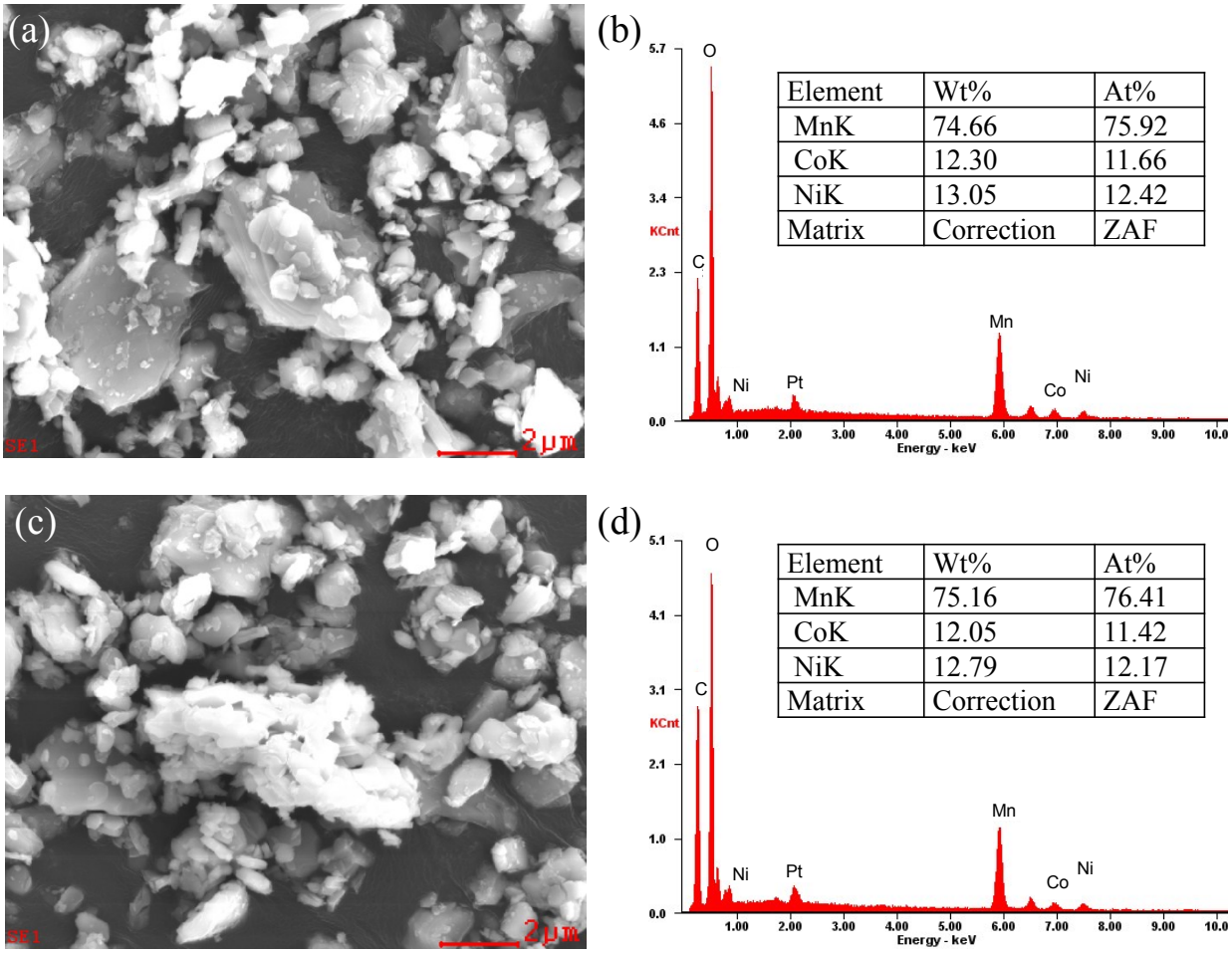

Figure S6. (a, c) FESEM images of c-HMLO at different two locations; (b, d) EDS patterns with the corresponding composition table.

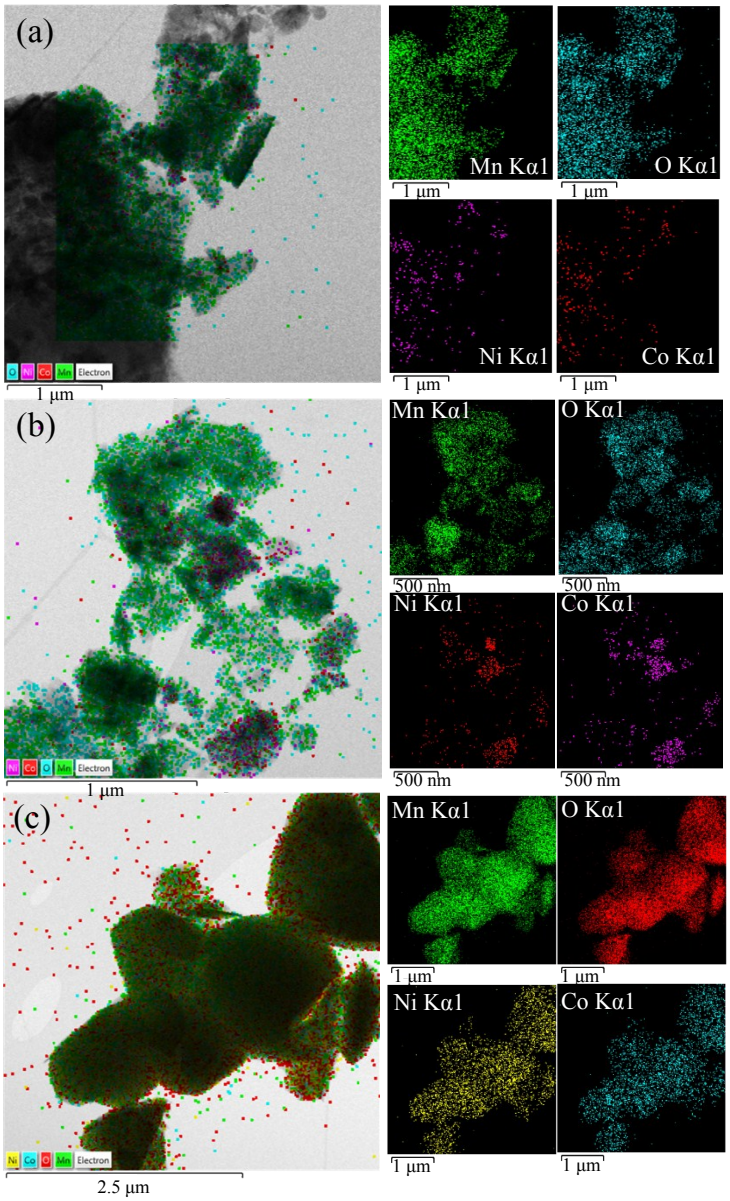

Figure S7. (a, b) STEM images of as-prepared m-HMLO with EDS elemental mapping of Mn (green), O (cyan), Ni (purple), and Co (red) in two different regions. (c) STEM image of as-prepared c-HMLO with EDS elemental mapping of Mn (green), O (red), Ni (yellow), and Co (cyan).

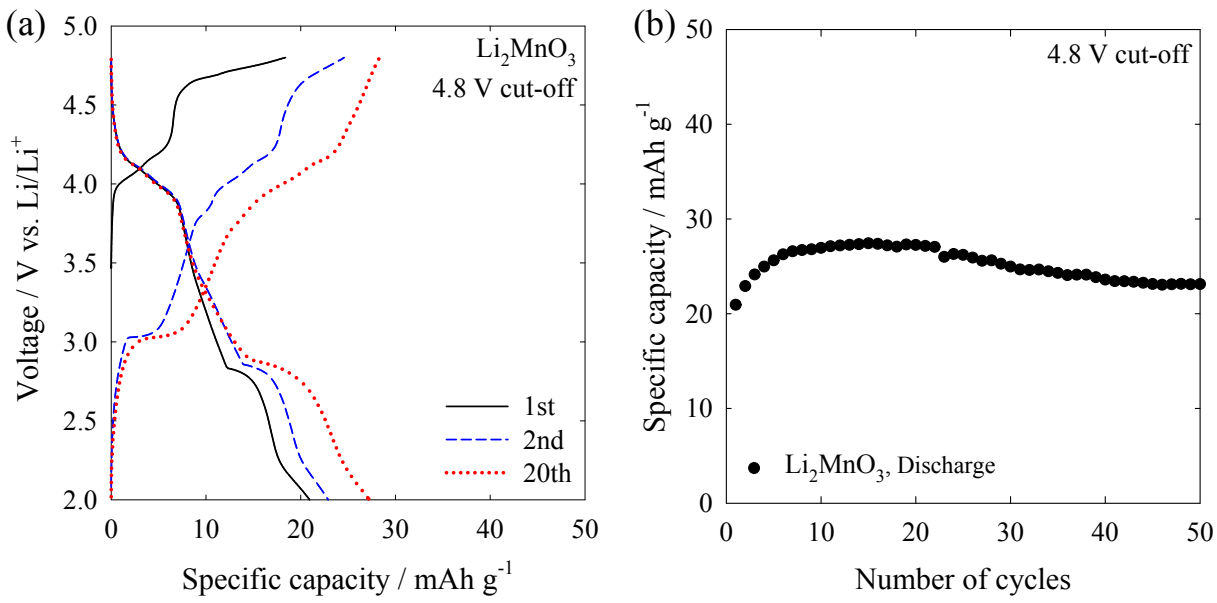

Figure S8. (a) Galvanostatic charge-discharge profiles of as-synthesized Li_2MnO_3, recorded in constant-current (CC) charging mode at a constant specific current of 13 mA g^{-1}, in the voltage range between 2.0 and 4.8 V *vs*. Li/Li^+ at 1st, 2nd, and 20th cycles. (b) Discharge (filled black circles) cyclic performance of as-synthesized Li_2MnO_3.

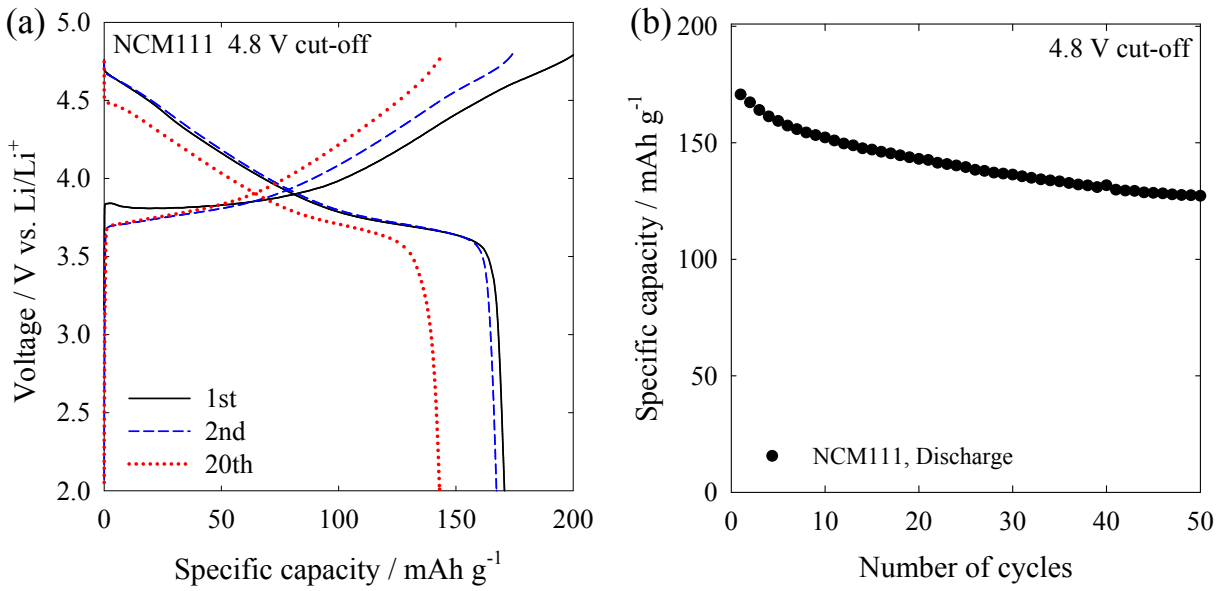

Figure S9. (a) Galvanostatic charge-discharge profiles of commercialized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NCM111) recorded in constant-current (CC) charging mode at a constant specific current of 25 mA g^{-1}, in the voltage range between 2.0 and 4.8 V *vs*. Li/Li^+ at 1st, 2nd, and 20th cycles. (b) Discharge (filled black circles) cyclic performance of commercialized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.

Table S1. Comparison of structural parameters of as-prepared c-HMLO obtained from Rietveld refinement and the atomic model of $Li_{1.67}Ni_{0.11}Co_{0.11}Mn_{0.67}\ Cu_{0.11}O_{2.67}$, obtained by density functional theory (DFT) calculation.

	a [Å]	*b* [Å]	*c* [Å]	*β* [°]
Rietveld	4.9369	17.0907	5.0268	109.29
DFT	5.0076	17.3247	5.0867	109.42

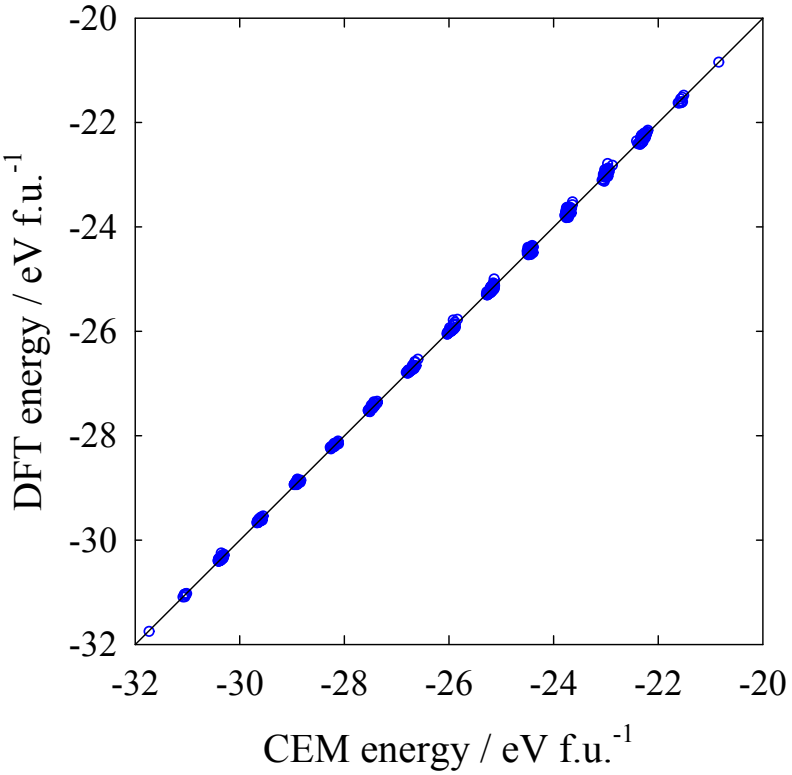

Figure S10. Total energy predicted by the cluster expansion method (CEM) *vs.* total energy calculated by density functional theory (DFT) for the same configuration (average root mean square error: 0.102 %).

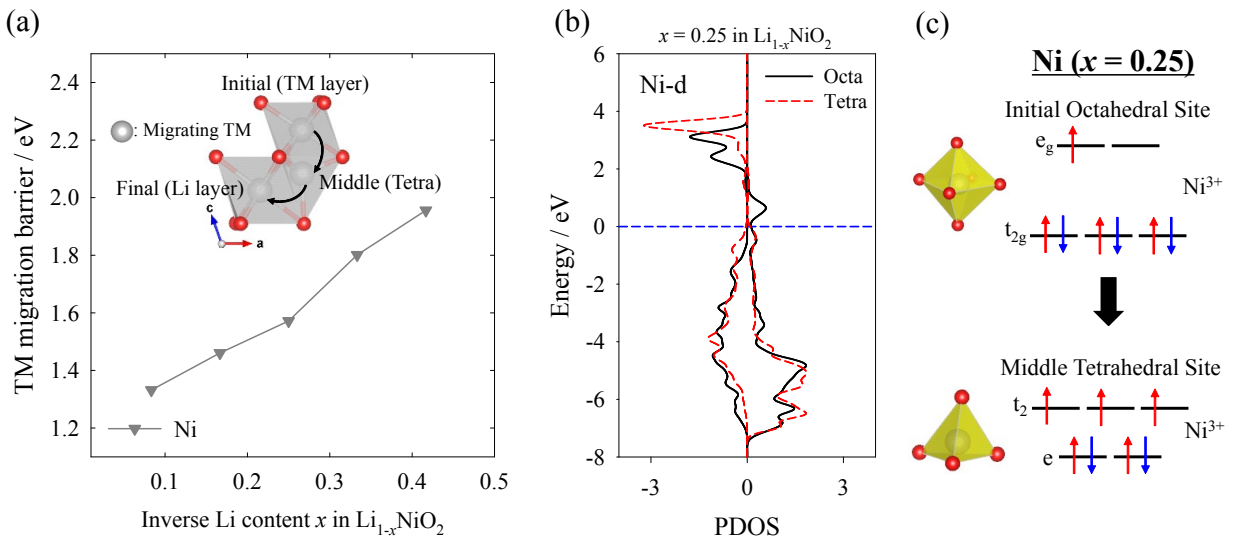

Figure S11. (a) Migration barriers of Ni ions with respect to the inverse Li content x in $Li_{1-x}NiO_2$ from the initial TM layer to the final Li layer *via* the middle tetrahedral site (inset). (b) PDOS for Ni d-orbital at the initial octahedral site (black solid line) and middle tetrahedral site (red dashed line) at $Li_{0.75}NiO_2$, where the Fermi level is 0.0 eV (blue dashed line). (c) Corresponding CFSDs of Ni d-orbitals at the initial octahedral site (upper) and middle tetrahedral site (lower) for $Li_{0.75}NiO_2$.