

Supporting Information

Understanding the electrochemical properties of Li-rich cathode materials from first-principles calculations

Tingting Cao,^a Chunsheng Shi,^a Naiqin Zhao,^{a,b} Chunnian He,^a Jiajun Li,^a Enzuo Liu^{,a,b}*

^a School of Materials science and Engineering and Tianjin Key Laboratory of composites and Functional Materials, Tianjin University, Weijin Road, No. 92, Tianjin 300072, P.R. China.

^b Collaborative Innovation Centre of Chemical Science and Engineering, Weijin Road, No. 92, Tianjin 300072, P.R. China.

*Address correspondence to ezliu@tju.edu.cn.

Table S1. The energy of the antiferromagnetic states and ferromagnetic states for Li-rich and LiMO₂. All energies are in eV.

		MY	M1	M2	M0.5	MF
Li-rich	FM	-421.885	-382.726	-344.575	-365.581	-302.475
	AFM	-422.207	-383.909	-342.780	-366.307	-311.383
LiMO ₂	FM	-411.464	-371.792	-334.137	-355.245	-298.810
	AFM	-412.176	-374.44	-336.982	-357.885	-305.393

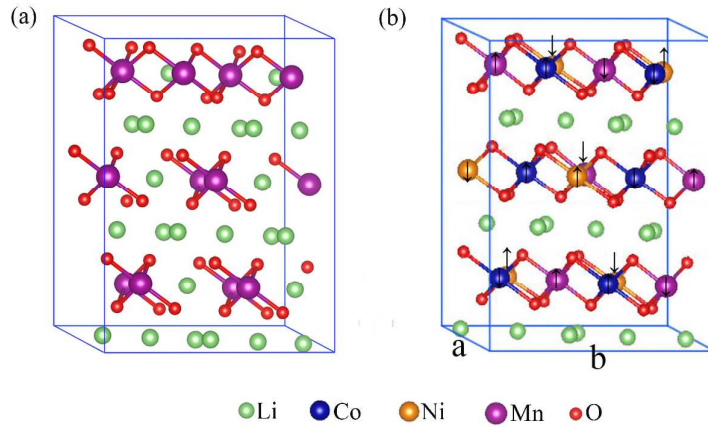


Figure S1. a)Structure model of Li₂MnO₃ with C2/m space group consists of 24 Li atoms in 2b, 2c, and 4h sites, 36 O atoms in 4i and 8j sites, and 12 Mn atoms in 8g sites. The parameters after geometry optimization: a=4.987, b=9.983, c=14.327 b) The antiferromagnetic state with alternative up and down spins along TM chains parallel to the b-axis in the LiMO₂ and the Li-rich.

Table S2. The average bond angle of the LiMO₂ phase in Li-rich and the pure LiMO₂. All angles are in degree. The angle is measured as the Figure S2 shown.

	O-Co-O	O-Ni-O	O-Mn-O
Li-rich	86.962	85.724	88.739
LiMO ₂	86.635	84.780	88.246

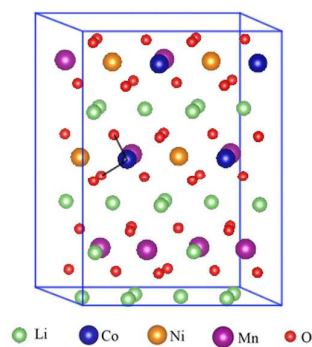


Figure S2. The schematic illustration of the O-TM-O bond angle

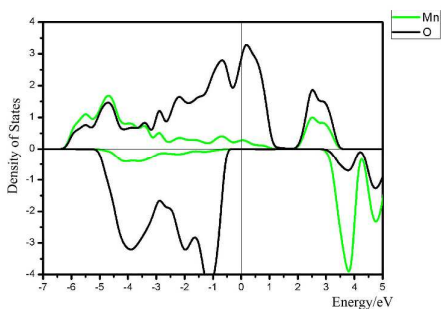


Figure S3. Partial density of states of Mn-3d and O-2p electrons in Li_2MnO_3 phase of the MF model of Li-rich materials. The O-2p states are the summation of the 2p states of 6 O around Mn. Compared to that in Li_2MnO_3 phase of the MY model of Li-rich materials, the DOS of Mn shifts left and the Fermi level is through the DOS of Mn, corresponding to the electronic loss of Mn during the deintercalation process.