Supporting Information for

Revealing the different effects of VIB transition metal X (X = Cr, Mo, W) on the electrochemical performance of Li-rich cathode Li_2MnO_3 by first-principles calculations

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Table S1. The energies of Li_2MnO_3 with different magnetic configurations.

Magnetic configuration	Energy (eV/f.u.)
ferromagnetic	-37.1728
antiferromagnetic	-37.1642

Table S2. Lattice parameters and volumes of Li_2MnO_3 and Li_2MnO_3 with Cr, Mo and W dilute doping.

System	Lattice parameter (Å)			Volume (Å^3)
	a	b	c	
Li_2MnO_3	5.010	8.660	5.091	208.223
Cr- Li_2MnO_3	5.015	8.659	5.094	208.441
Mo- Li_2MnO_3	5.040	8.690	5.107	210.642
W- Li_2MnO_3	5.036	8.729	5.104	211.633

Table S3. The average Bader charges of doped TM, Mn and O near the TM in TM-Li_xMnO_3 (TM = Cr, Mo, W) systems.

System	x	Average Bader charge (e)		
		Mn	O	TM (Cr, Mo, W)
Li_xMnO_3	2	+1.897	-1.226	+1.897
	1.75	+1.903	-1.066	+1.899
	1.5	+1.928	-0.975	+1.928
	1.25	+1.940	-0.991	+1.938
	1	+1.960	-0.954	+1.960
Cr-Li_xMnO_3	2	+1.897	-1.234	+1.982
	1.75	+1.912	-1.034	+2.131
	1.5	+1.933	-0.984	+2.115
	1.25	+1.928	-0.993	+2.145
	1	+1.958	-0.933	+2.117
Mo-Li_xMnO_3	2	+1.867	-1.294	+2.544
	1.75	+1.889	-1.132	+2.726
	1.5	+1.917	-1.087	+2.732
	1.25	+1.918	-1.104	+2.725
	1	+1.973	-1.066	+2.747
W-Li_xMnO_3	2	+1.779	-1.264	+2.962
	1.75	+1.889	-1.177	+2.999
	1.5	+1.914	-1.136	+3.003
	1.25	+1.918	-1.149	+2.985
	1	+1.952	-1.112	+3.001

Table S4. The average formation enthalpies of different Li vacancies in fully lithiated

Li_2MnO_3 and TM-Li_2MnO_3(TM=Cr, Mo, W)

System	Site	Formation enthalpy (eV)
Li_2MnO_3	2*b*	4.78
	2*c*	4.67
	4*h*	4.62
Cr-Li_2MnO_3	2*b*	4.30
	2*c*	4.21
	4*h*	4.18
Mo-Li_2MnO_3	2*b*	2.89
	2*c*	2.79
	4*h*	2.75
W-Li_2MnO_3	2*b*	2.55
	2*c*	2.43
	4*h*	2.43

Table S5. The average formation enthalpies of O vacancies around TM at different delithiation stages in TM-Li_2MnO_3(TM=Cr, Mo, W)

System	x	Average formation enthalpy (eV)
Li_xMnO_3	2	2.59
	1.75	0.45
	1.5	0.10
	1.25	-0.07
	1	-0.63
Cr-Li_xMnO_3	2	2.46
	1.75	-0.18
	1.5	-0.28
	1.25	-0.53
	1	-1.20
Mo-Li_xMnO_3	2	3.40
	1.75	1.26
	1.5	0.29
	1.25	0.04
	1	-0.74
W-Li_xMnO_3	2	3.71
	1.75	1.68
	1.5	0.68
	1.25	0.44
	1	-0.56

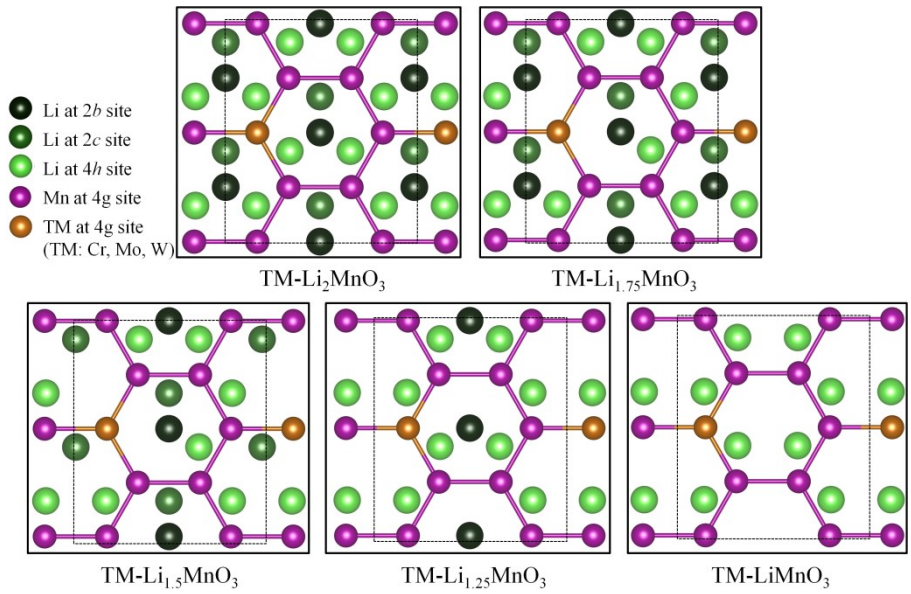

Figure S1. Illustrations of the partially delithiated structures of TM-Li_xMnO_3 (x = 2, 1.75, 1.5, 1.25, 1). The black dashed box represents a structural period. The delithiation sequence is described as follows: (1) some Li ions at the 4*h* sites are extracted ($1.75 \le x < 2$), (2) some Li ions at the 2*b* sites are extracted ($1.5 \le x < 1.75$), (3) half of the Li ions at the 2*c* sites are extracted and the other half of Li ions at the 2*c* sites migrate to the 4*h* sites ($1.25 \le x < 1.5$), (4) all Li ions at the 2b sites are extracted ($1 \le x < 1.25$).

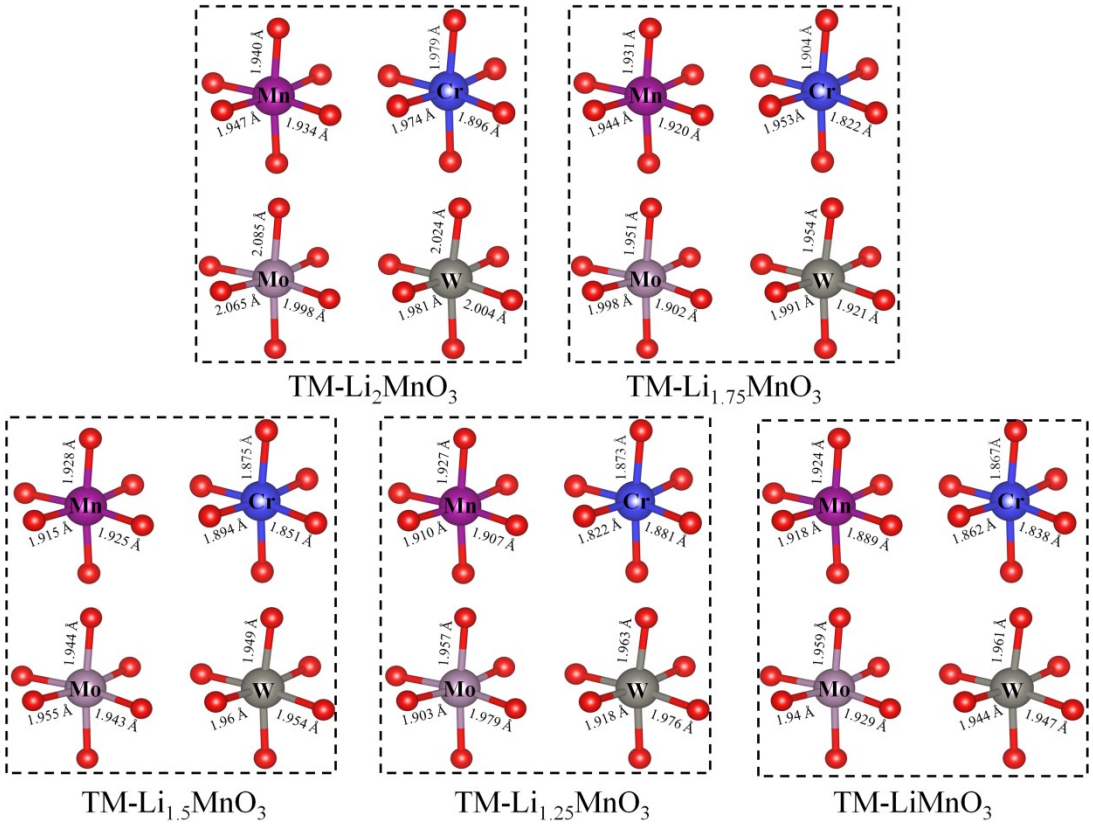

Figure S2. The Bond lengths of TM-O at different stages of delithiation of TM-Li_xMnO_3 (x = 2, 1.75, 1.5, 1.25, 1).

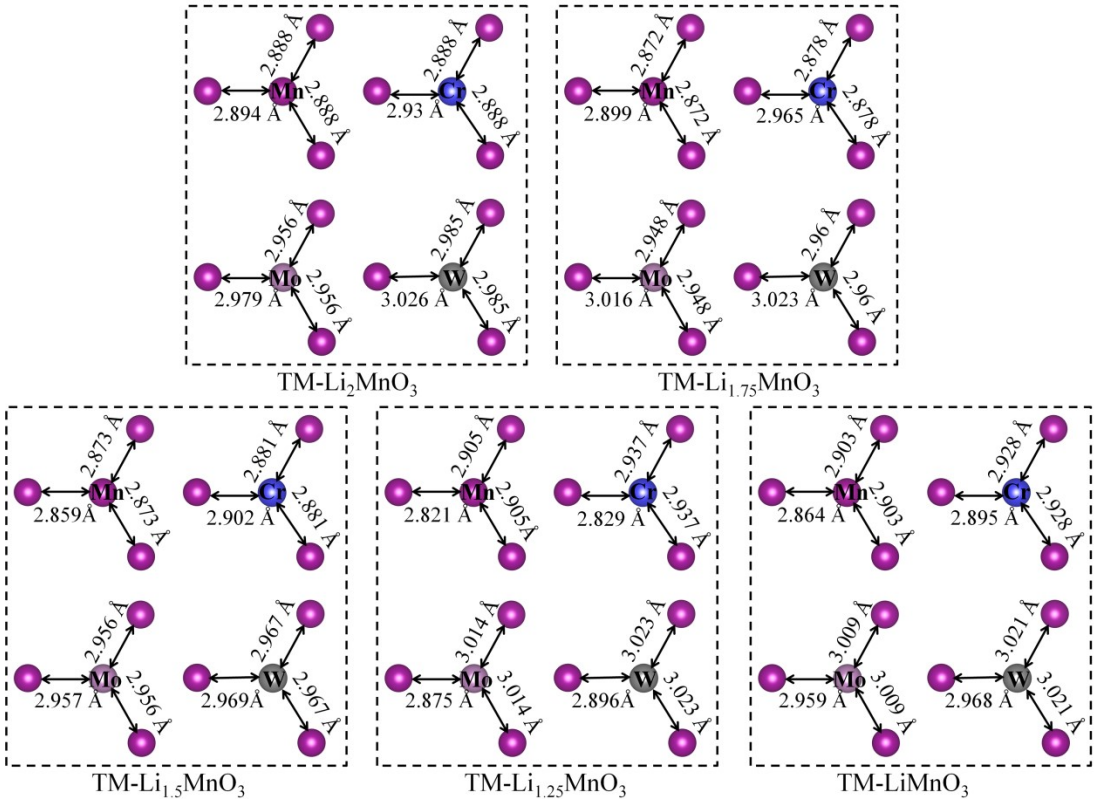

Figure S3. The distances between TM and its surrounding Mn at different stages of delithiation of TM-Li_xMnO_3 (x = 2, 1.75, 1.5, 1.25, 1).

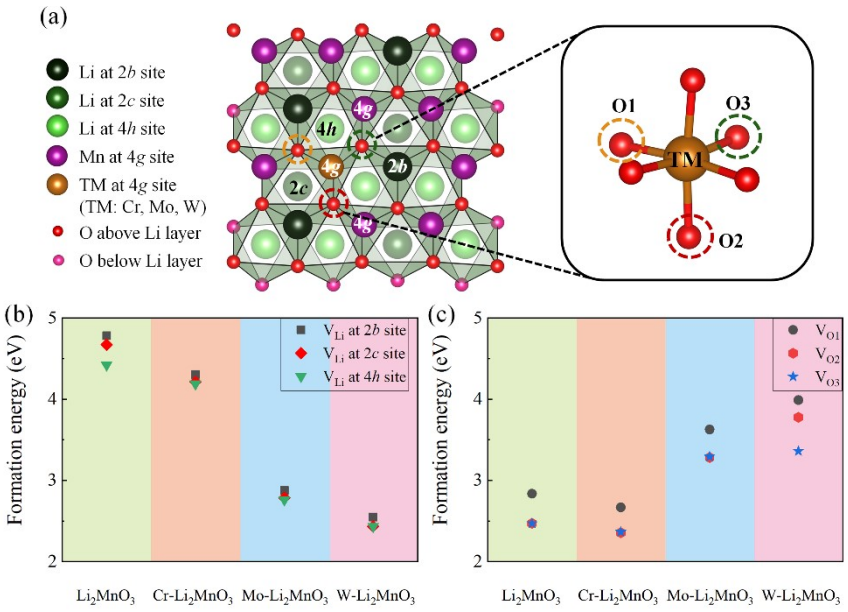

Figure S4. (a) Illustrations of the nearest Li and O sites near the TM doping site in TM-Li_2MnO_3 (TM=Cr, Mo, W). (b) Formation enthalpies of different Li vacancies in TM- Li_2MnO_3. (c) Formation enthalpies of different O vacancies in TM- Li_2MnO_3.

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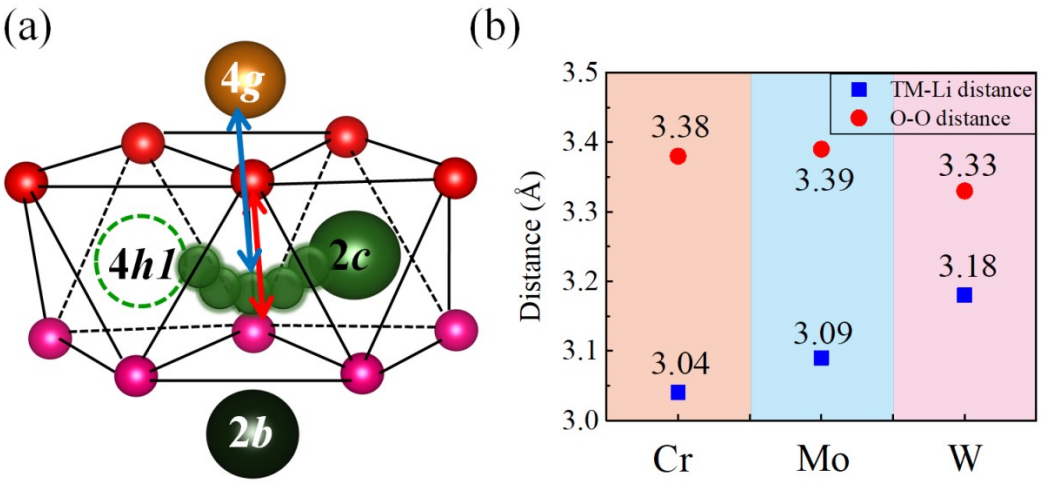

Figure S5. (a) Illustrations of the maximum distance between the mobile Li and TM in path 2*c* - 4*h*1 (shown by the blue arrow), and the maximum distance between O in O-O dumbbell structure (shown by the red arrow). (b) The values of the distances.