Electronic Supplementary Information

Charge-transfer descriptor on the cycle performance of β-Li_2MO_3 cathode: Role of oxygen dimer

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Table S1. Phase stability (E^{hull}) of 15 β-Li_2MO_3 materials.

Target comp	Competing species	E^{hull} (meV atom^{-1})
Li_2CrO_3	1/2 Li_3CrO_4 + 1/2 $LiCrO_2$	25.9
Li_2MnO_3	Li_2MnO_3 (polymorph, C2/m)	0.7
Li_2FeO_3	1/2 Li_2O_2 + $LiFeO_2$	5.4
Li_2CoO_3	1/5 $Li_7Co_5O_{12}$ + 3/10 Li_2O_2	26.4
Li_2NiO_3	Li_2NiO_3 (polymorph, C2/m)	1.0
Li_2MoO_3	1/3 Li_4MoO_5 + 1/3 Li_2MoO_4 + 1/3 Mo	17.7
Li_2TcO_3	Li_2TcO_3 (polymorph, C2/c)	34.3
Li_2RuO_3	Li_2RuO_3 (polymorph, C2/m)	0.4
Li_2RhO_3	Li_2RhO_3 (polymorph, C2/m)	0.8
Li_2PdO_3	Li_2PdO_3 (polymorph, C2/m)	0.1
Li_2WO_3	1/3 Li_2WO_4 + 1/3 Li_4WO_5 + 1/3 W	144.5
Li_2ReO_3	3/14 $LiReO_4$ + 5/14 Li_5ReO_6 + 3/7 Re	92.2
Li_2OsO_3	1/3 Li_5OsO_6 + 1/3 $LiOsO_3$ + 1/3 Os	39.4
Li_2IrO_3	Li_2IrO_3 (polymorph, C2/m)	-5.0
Li_2IPtO_3	Li_2PtO_3 (polymorph, C2)	2.7

	PBE	PBE0	HSE06	Experiment
***U* (eV)**	6.704	8.809	8.032	-
Δ (eV)	7.187	9.228	8.459	-
R^O	0.189	0.661	0.674	-
Voltage (V)	3.242	3.883	3.860	3.964

Table S2. *U*, Δ, R^O and voltage values of β–Li_2IrO_3.

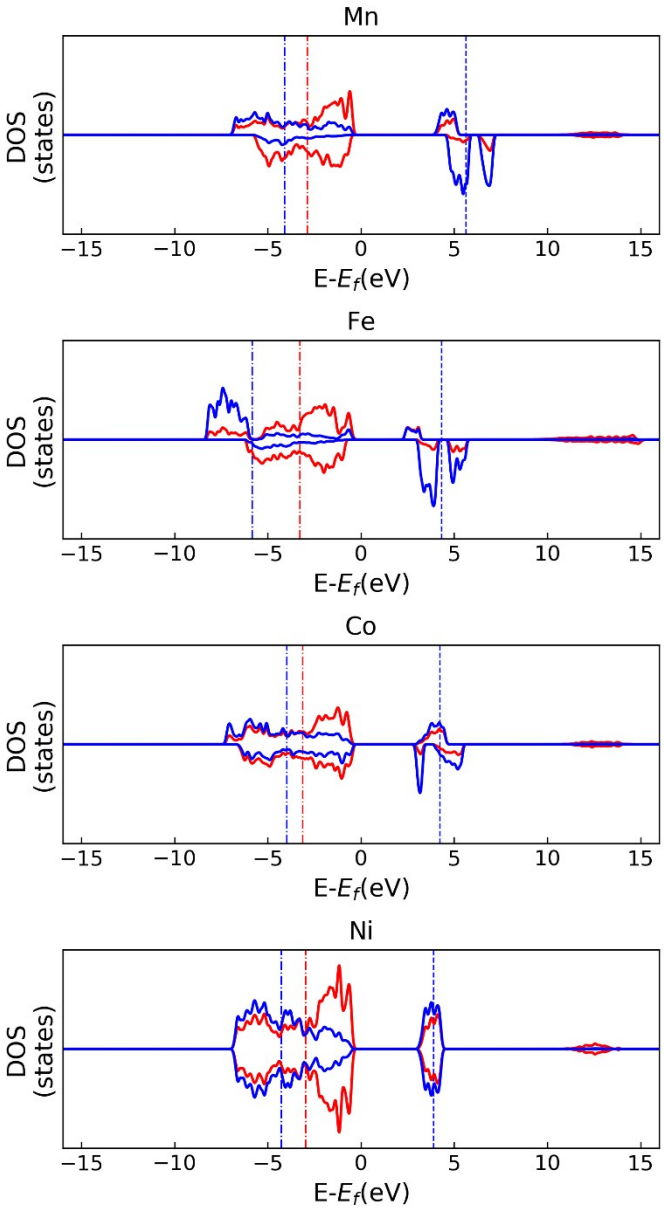

Fig. S1. Partial density of states (PDOS) of β-Li_2MO_3 of 3d TMs. Vertical dashed line represents band centers.

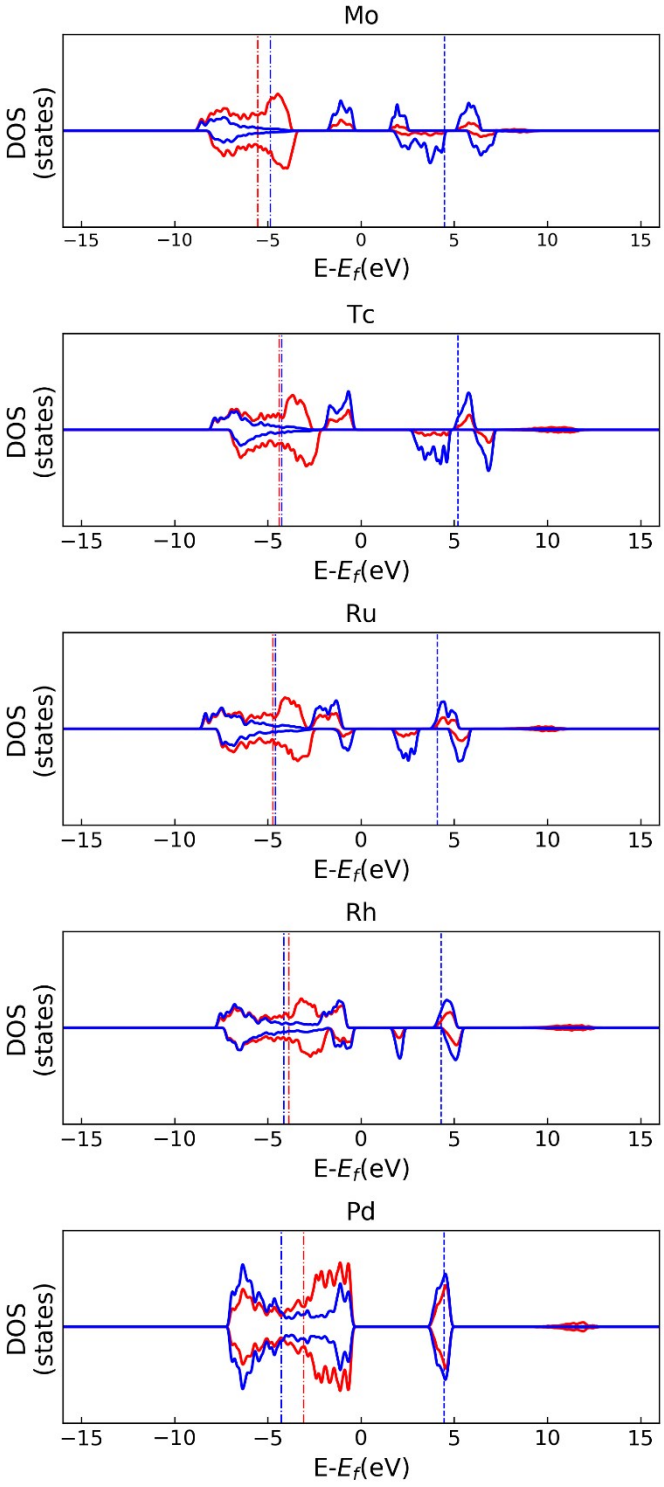

Fig. S1. (Continued) Partial density of states (PDOS) of β-Li_2MO_3 of 4d TMs. Vertical dashed line represents band centers.

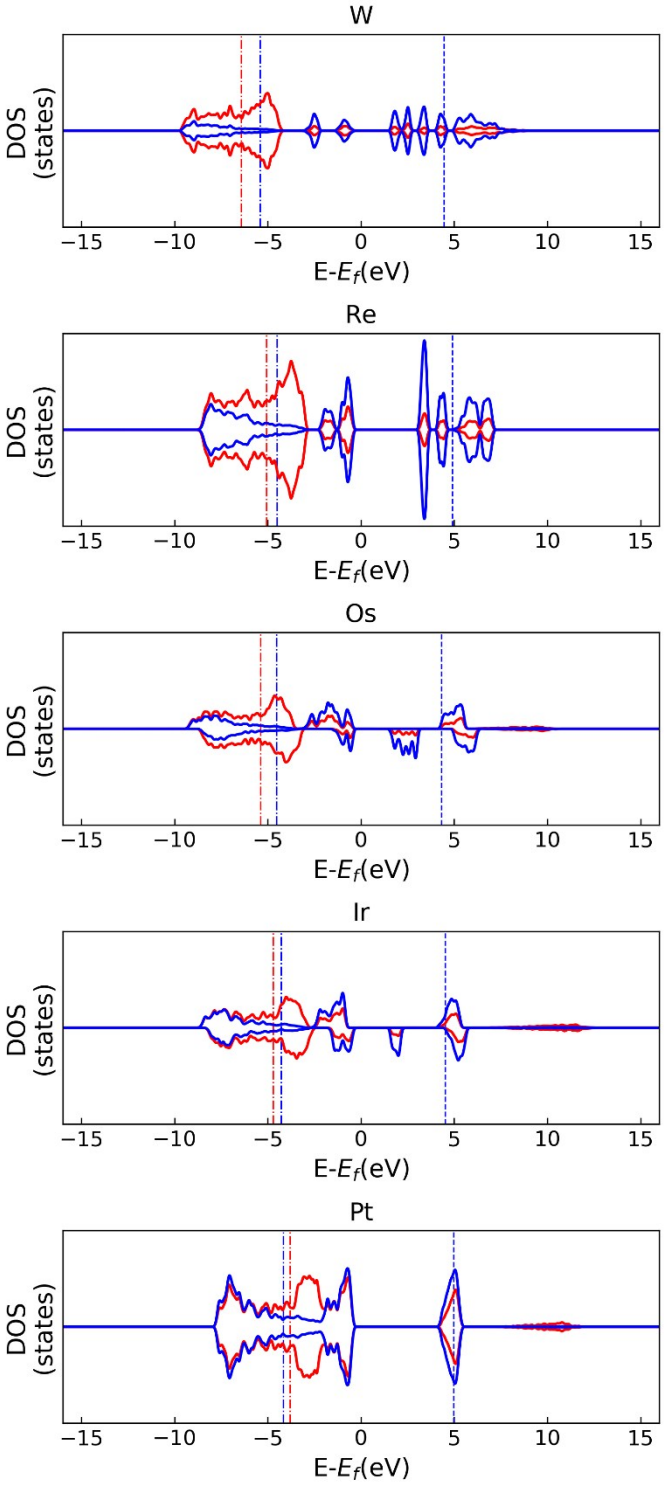

Fig. S1. (Continued) Partial density of states (PDOS) of β-Li_2MO_3 of 5d TMs. Vertical dashed line represents band centers.

Table S3. Band gap and distortion index of β-Li_2MO_3.

	Band gap of β-Li_2MO_3	**Distortion index(x 10^4) of β-Li_2MO_3**
Mn	3.84	0.05
Fe	2.19	37.487
Co	2.76	3.578
Ni	2.92	0.021
Mo	1.45	2.76
Tc	2.53	0.095
Ru	1.61	5.734
Rh	1.49	0.684
Pd	3.51	0.035
W	1.45	8.294
Re	2.95	2.448
Os	1.39	0.487
Ir	1.43	0.734
Pt	4.02	0.034

Table S4. The charge variation of TM (Q^M) and oxygen (Q^O) when β-Li_2MO_3 is charged to β-MO_3 for M = Mo, Tc, Ru, Rh, W, Re, Os, and Ir, and to β'-MO_3 for M = Mn, Fe, Co, Ni and Pd.

	Q^M	Q^O
Mn	-0.935	7.222
Fe	-0.032	6.213
Co	-0.815	7.045
Ni	-0.494	6.360
Mo	2.405	3.424
Tc	2.010	3.865
Ru	1.962	3.651
Rh	0.552	5.067
Pd	-2.091	7.383
W	3.187	2.113
Re	2.917	1.832
Os	2.565	2.893
Ir	1.979	3.862
Pt	0.802	4.302

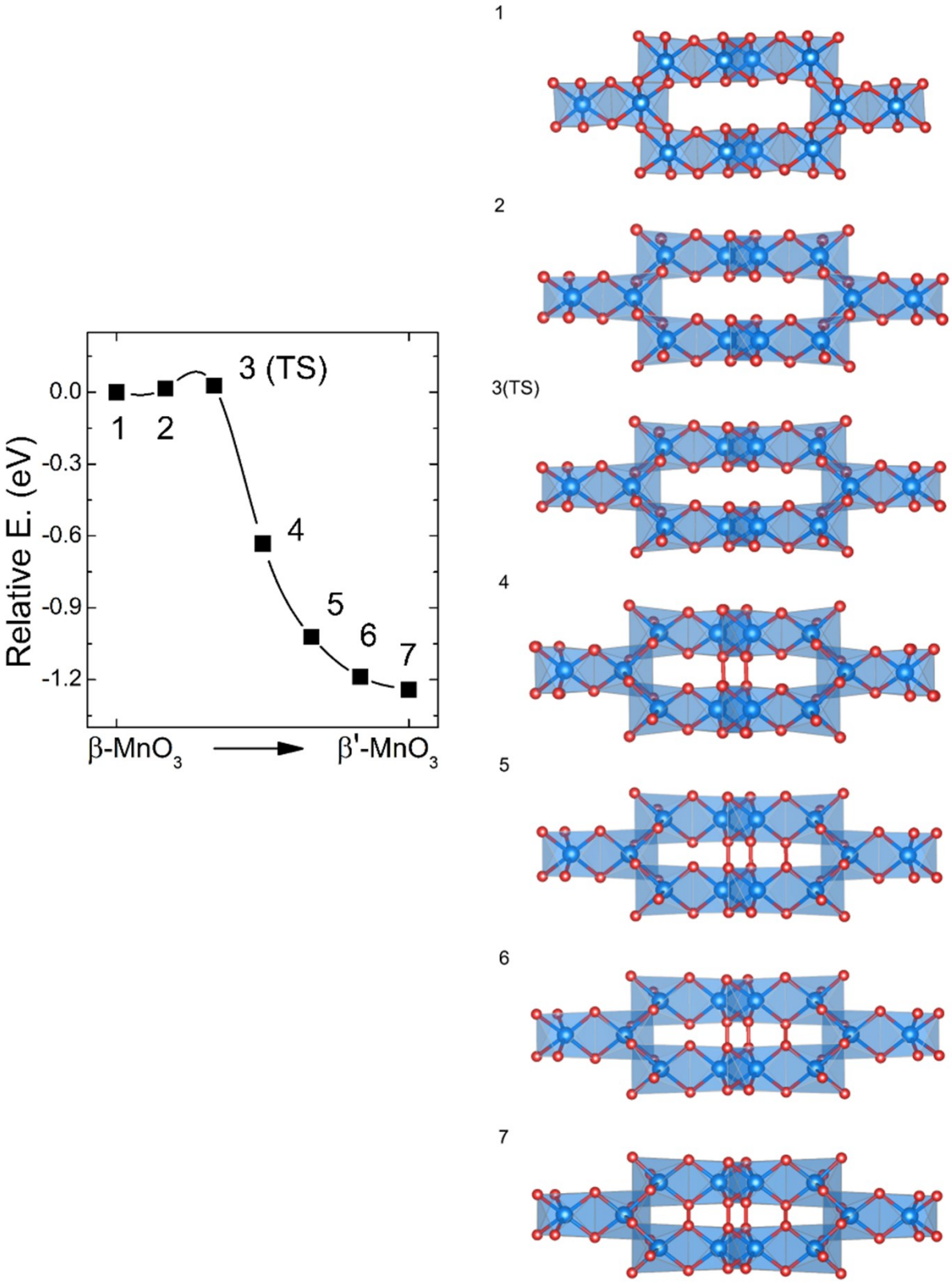

Fig. S2. Crystal structure of intermediate states for the β–to–β' phase transformation.

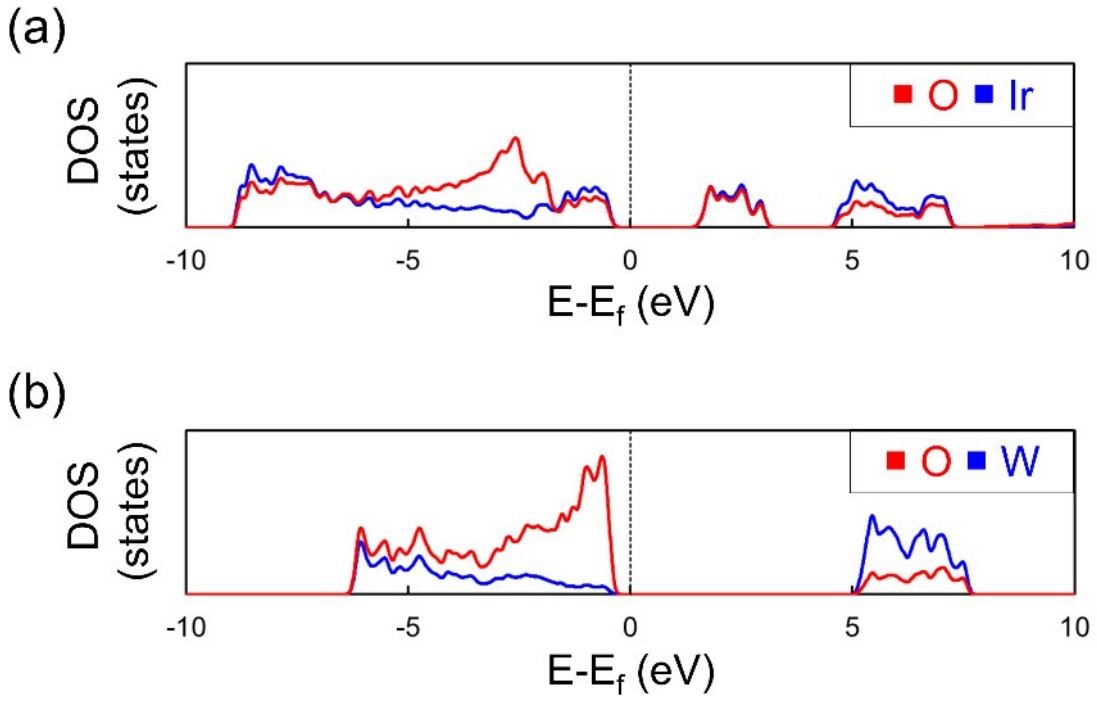

Fig. S3. Partial density of states (PDOS) results: (a) β-WO_3 and (b) β-IrO_3.

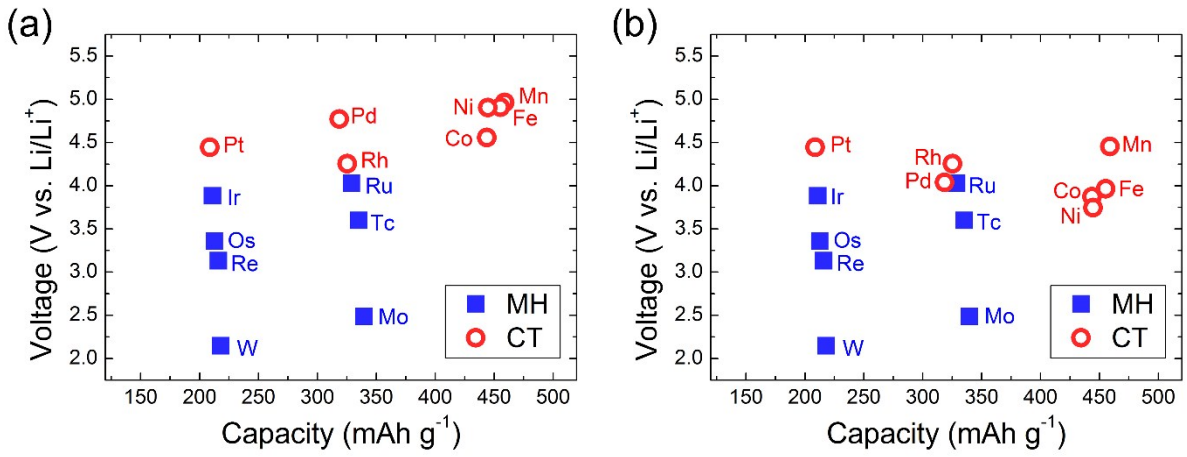

Fig. S4. (a) The average voltage when β-Li_2MO_3 is charged to β-MO_3 and theoretical capacity. (b) The average voltage when β-Li_2MO_3 is charged to β-MO_3 and theoretical capacity.