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Understanding the electrochemical properties of Mg doped Li_2MnO_3: First-principles calculations

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System	Lattice parameter (Å)		
	a	b	c
Li_2MnO_3	10.020	8.660	10.181
Mg_{2b}-Li_2MnO_3	10.024	8.663	10.186
Mg_{4h}-Li_2MnO_3	10.024	8.662	10.186

Table S1. Calculated lattice parameters of the supercells for pristine and Mg-doped Li_2MnO_3.

System	Element	Atoms	Formation energy (eV)
Mg_{2b}-Li_xMnO_3	Li_{4h}	(a)	3.84
		(b)	3.42
		(c)	3.91
Li_xMnO_3	Li_{4h}	(a)	4.62
		(b)	4.59
		(c)	4.68

Table S2. Calculated formation energies of different Li_{4h} vacancies in Fig. S2.

System	x	Bader charge (e) of O						
		O1	O2	O3	O4	O5	O6	O
Mg_{2b}-Li_xMnO_3	2	-1.276	-1.282	-1.276	-1.276	-1.282	-1.276	-1.278
		(-1.205)	(-1.230)	(-1.201)	(-1.204)	(-1.230)	(-1.201)	(-1.212)
	1.75	-1.236	-1.199	-1.190	-1.236	-1.199	-1.190	-1.208
		(-1.176)	(-1.112)	(-1.109)	(-1.176)	(-1.112)	(-1.109)	(-1.132)
	1.5	-1.222	-1.190	-1.185	-1.222	-1.190	-1.185	-1.199
		(-1.162)	(-1.115)	(-1.114)	(-1.162)	(-1.115)	(-1.114)	(-1.131)
	1.25	-1.140	-1.190	-1.140	-1.140	-1.190	-1.140	-1.156
		(-1.055)	(-1.091)	(-1.055)	(-1.055)	(-1.090)	(-1.055)	(-1.067)
	1	-1.029	-1.144	-1.082	-1.029	-1.144	-1.082	-1.085
		(-1.072)	(-1.072)	(-1.042)	(-1.042)	(-1.042)	(-1.042)	(-1.051)
Mg_{4h}-Li_xMnO_3	2	-1.302	-1.239	-1.238	-1.302	-1.239	-1.239	-1.260
		(-1.230)	(-1.201)	(-1.204)	(-1.230)	(-1.201)	(-1.204)	(-1.212)
	1.75	-1.189	-1.226	-1.225	-1.189	-1.226	-1.226	-1.213
		(-1.112)	(-1.109)	(-1.038)	(-1.112)	(-1.109)	(-1.039)	(-1.086)
	1.5	-1.189	-1.209	-1.123	-1.189	-1.209	-1.209	-1.173
		(-1.115)	(-1.114)	(-0.877)	(-1.115)	(-1.114)	(-0.877)	(-1.036)
	1.25	-1.185	-1.121	-1.008	-1.185	-1.121	-1.121	-1.105
		(-1.090)	(-1.055)	(-0.934)	(-1.090)	(-1.055)	(-0.934)	(-1.027)
	1	-1.083	-1.033	-1.014	-1.083	-1.033	-1.033	-1.049
		(-1.090)	(-1.050)	(-0.906)	(-1.090)	(-1.050)	(-0.906)	(-1.015)

Table S3. Bader charges of O around Mg/Li in each delithiation stage. The values in brackets are the Bader charges of O anions in the undoped Li_2MnO_3. The last column shows the averaged value of O.

System	x	Bader charge (e) of Mn						
		Mn1	Mn2	Mn3	Mn4	Mn5	Mn6	Mn
Mg_{2b}-Li_xMnO_3	2	+1.852	+1.852	+1.793	+1.852	+1.852	+1.793	+1.832
		(+1.860)	(+1.860)	(+1.860)	(+1.860)	(+1.860)	(+1.860)	(+1.860)
	1.75	+1.843	+1.860	+1.868	+1.860	+1.843	+1.856	+1.855
		(+1.852)	(+1.864)	(+1.876)	(+1.864)	(+1.852)	(+1.861)	(+1.861)
	1.5	+1.858	+1.868	+1.874	+1.868	+1.858	+1.867	+1.866
		(+1.863)	(+1.870)	(+1.884)	(+1.870)	(+1.863)	(+1.873)	(+1.870)
	1.25	+1.868	+1.868	+1.882	+1.868	+1.868	+1.882	+1.873
		(+1.873)	(+1.874)	(+1.882)	(+1.874)	(+1.873)	(+1.882)	(+1.876)
	1	+1.873	+1.873	+1.891	+1.873	+1.873	+1.890	+1.879
		(+1.881)	(+1.881)	(+1.881)	(+1.881)	(+1.886)	(+1.886)	(+1.883)
Mg_{4h}-Li_xMnO_3	2	+1.787	+1.787	+1.822	+1.822	–	–	+1.806
		(+1.860)	(+1.860)	(+1.860)	(+1.860)	–	–	(+1.860)
	1.75	+1.846	+1.846	+1.823	+1.823	–	–	+1.831
		(+1.852)	(+1.852)	(+1.864)	(+1.864)	–	–	(+1.858)
	1.5	+1.863	+1.863	+1.837	+1.837	–	–	+1.850
		(+1.863)	(+1.863)	(+1.870)	(+1.870)	–	–	(+1.866)
	1.25	+1.867	+1.867	+1.860	+1.860	–	–	+1.864
		(+1.873)	(+1.873)	(+1.874)	(+1.874)	–	–	(+1.874)
	1	+1.874	+1.874	+1.867	+1.867	–	–	+1.871
		(+1.879)	(+1.879)	(+1.881)	(+1.881)	–	–	(+1.881)

Table S4. Bader charges of Mn around Mg/Li in each delithiation stage. The values in brackets are the Bader charges of Mn anions in the undoped Li_2MnO_3. The serial numberS for Mn are shwn in Fig. S4 and the last column shows the averaged value of Mn.

System	x	Formation energy (eV)
Li_xMnO_3	2	2.61
	1.75	0.70
	1.5	0.34
	1.25	0.06
	1	-0.38
Mg_{2b}-Li_xMnO_3	2	3.63
	1.75	1.52
	1.5	1.27
	1.25	0.50
	1	0.06
Mg_{4h}-Li_xMnO_3	2	3.65
	1.75	1.36
	1.5	0.96
	1.25	0.45
	1	-0.02

Table S5. Average formation energy of O vacancies around the doping site at different delithiation stages in Li_xMnO_3, Mg_{2b}-Li_xMnO_3 and Mg_{4h}-Li_xMnO_3.

Path	Diffusion barrier (eV)		
	Li_2MnO_3	Mg_{2b}-Li_2MnO_3	Mg_{4h}-Li_2MnO_3
2c-4h1	0.62	0.59	0.79
2c-4h2	0.88	0.78	0.82
2b-4h1	0.78	0.84	0.86

Table S6. The energy barrier for Li vacancy diffusion along path 2c-4h1, path 2c-4h2 and path 2b-4h1 in Li_2MnO_3, Mg_{2b}-Li_2MnO_3 and Mg_{4h}-Li_2MnO_3.

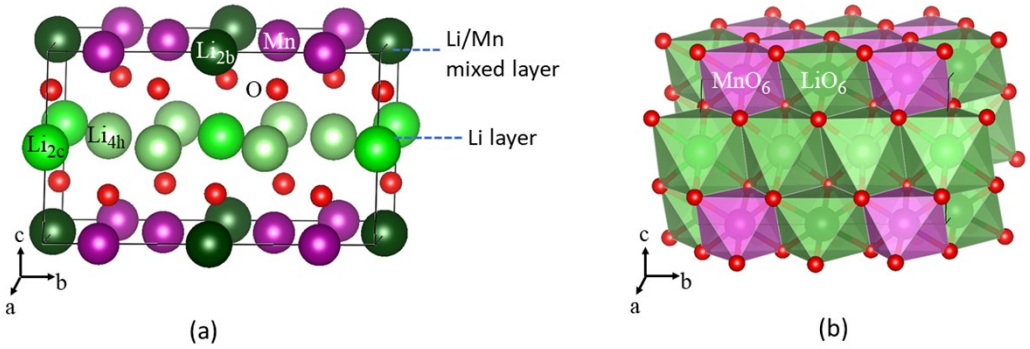

Fig. S1. (a) Monoclinic Li_2MnO_3 structure with a C2/m space group and the atomic occupation positions of Li, Mn and O atoms. (b) Illustration of the MnO_6 and LiO_6 octahedra.

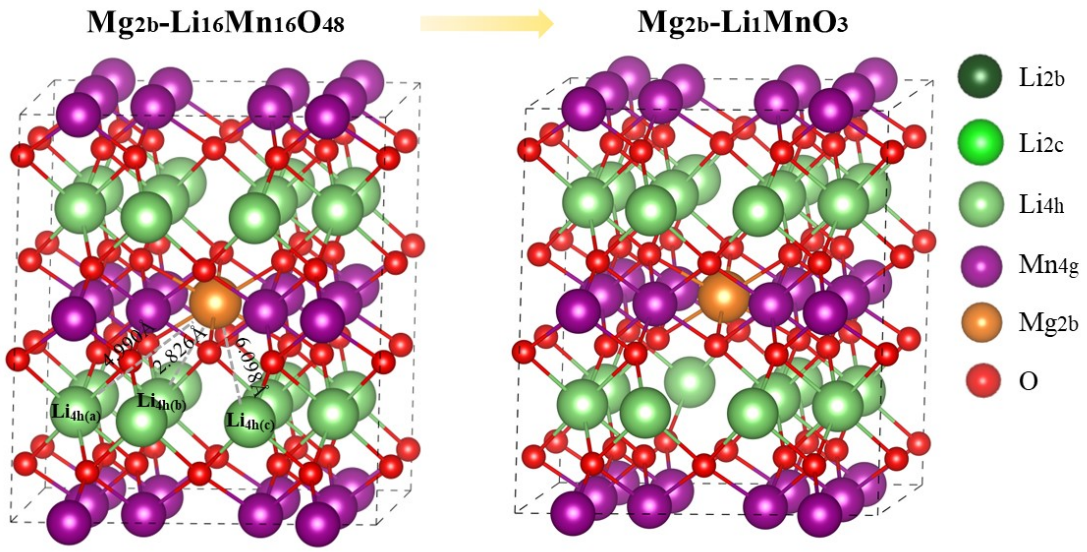

Fig. S2. The three un-equivalent 4h Li in the vicinity of doped Mg in Mg_{2b}-Li_xMnO_3.

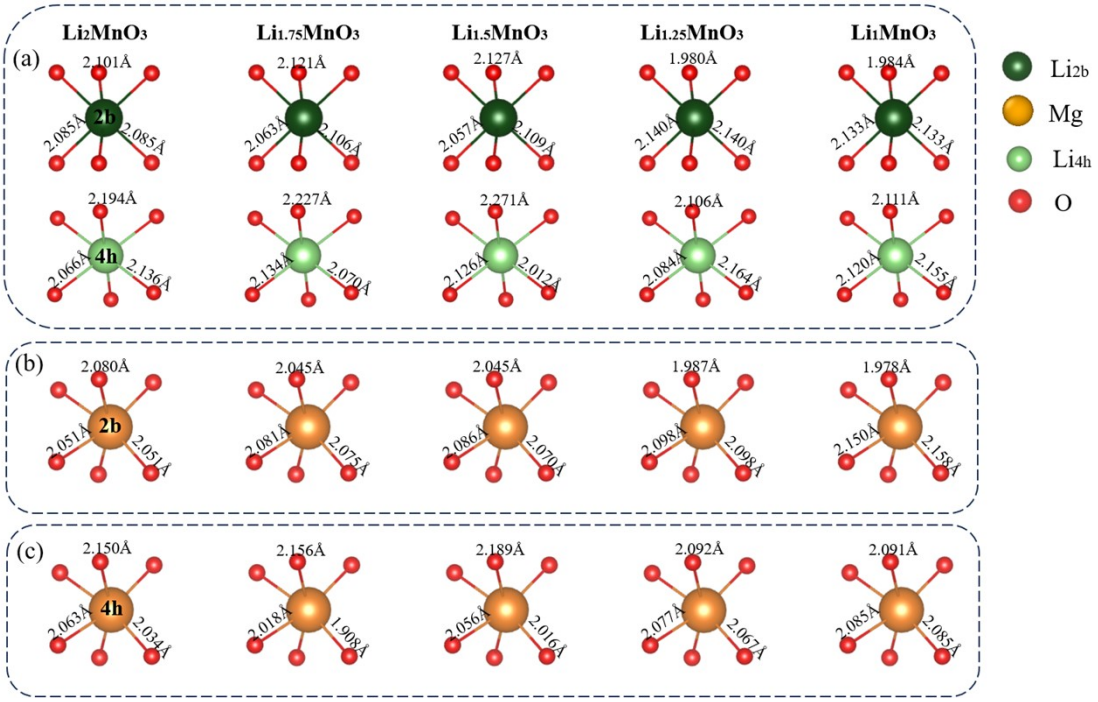

Fig. S3. Bond lengths of Li-O or Mg-O in (a) Li_xMnO_3, (b) Mg_{2b}-Li_xMnO_3, and (c) Mg_{4h}-Li_xMnO_3 (x = 2, 1.75, 1.5, 1.25, and 1).

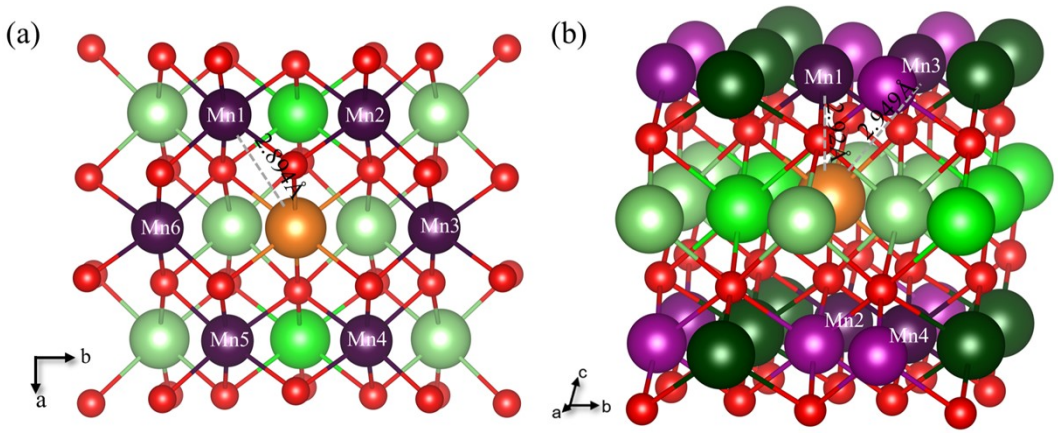

Fig. S4. Schematic shows the nearby by Mn ions of Mg in (a)Mg_{2b}-Li_2MnO_3 and (c) Mg_{4h}-Li_2MnO_3.

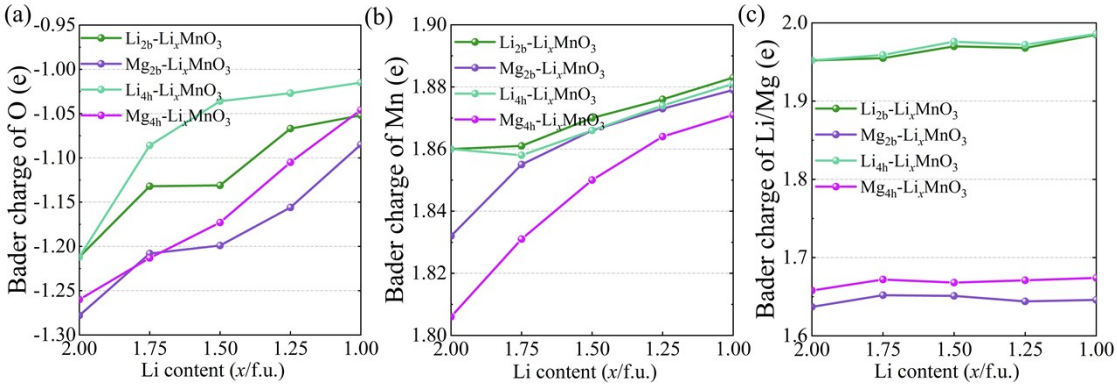

Fig. S5 The average Bader charge of (a) O in LiO_6 or MgO_6 octahedron, (b) Mn around Li or Mg, and (c) Li and doped Mg at different delithiation stages of Li_xMnO_3 (x = 2, 1.75, 1.5, 1.25, and 1).

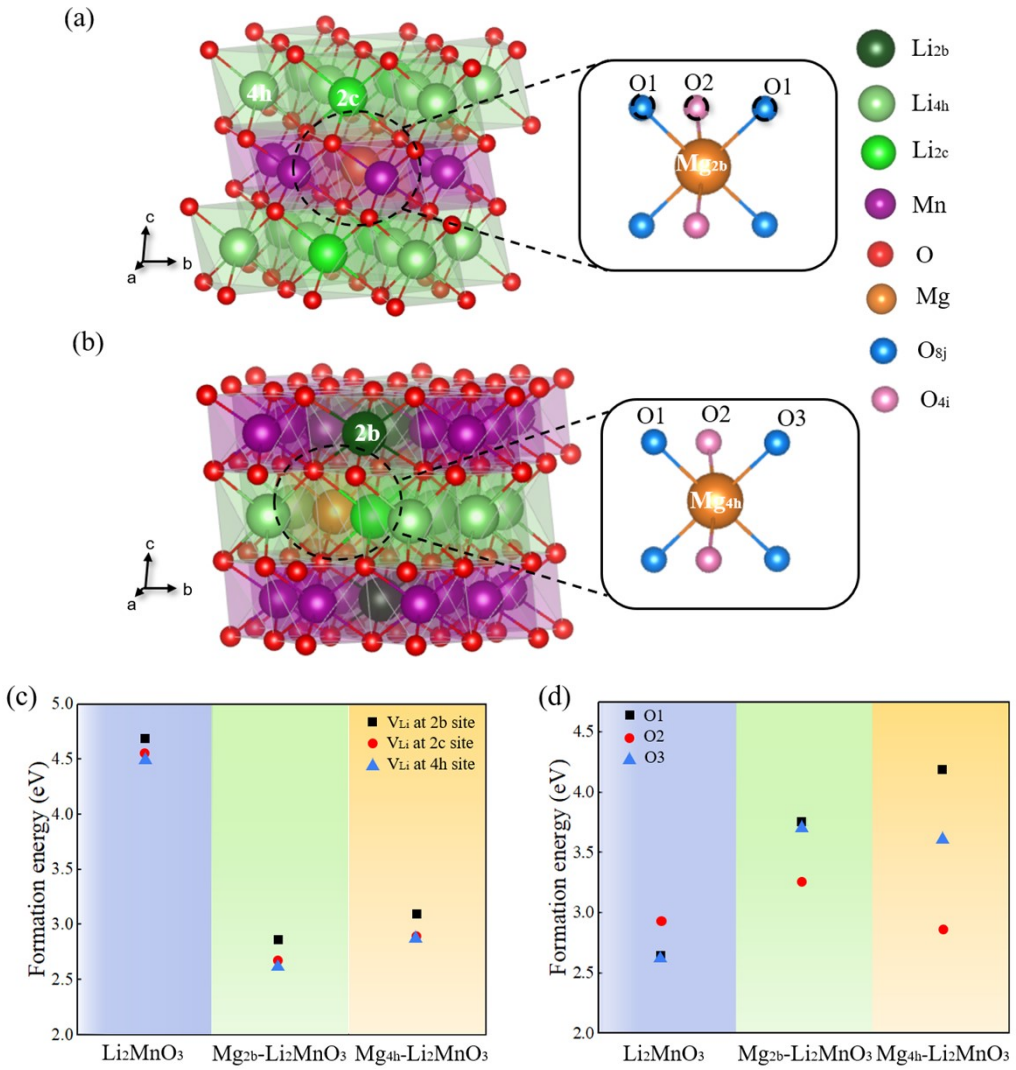

Fig. S6. (a) Illustration of different oxygen atoms (O1 and O2) near the doping site in the Mg_{2b}-Li_2MnO_3. (b) Illustration of different oxygen atoms (O1, O2, and O3) near the doping site in the Mg_{4h}-Li_2MnO_3. (c) Formation energies of different Li vacancies in pure and Mg doped Li_2MnO_3. (d) Formation energies of different O vacancies in pure and Mg doped Li_2MnO_3.