Polyhedral Perspective on Capacity Limit of Cathode Compounds for Lithium-ion Battery: A Case Study for Li_6CoO_4

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I. Prototype of tetrahedron structured Li_2O and octahedron structured Li_2O_2

In tetrahedron structured Li_2O, the prototype is cubic lattice with space group $Fm\bar{3}m$, where all tetrahedral sites are occupied by Li within ABC stacked oxygen sublattice, shown in Fig.S1-**a**. However, within AB stacked oxygen sublattice, half tetrahedra share face with the other half, seen in Fig.S1-**c**, that would be energy unfavorable because the very strong repulsion between face-sharing tetrahedra while attraction between corner- or edge- sharing tetrahedra.[1] In addition, face sharing octahedra may only energy favor for metal ions totally disordered because the shared face is a strong geometric restriction, seen in Fig. S1-**b** and **d**.

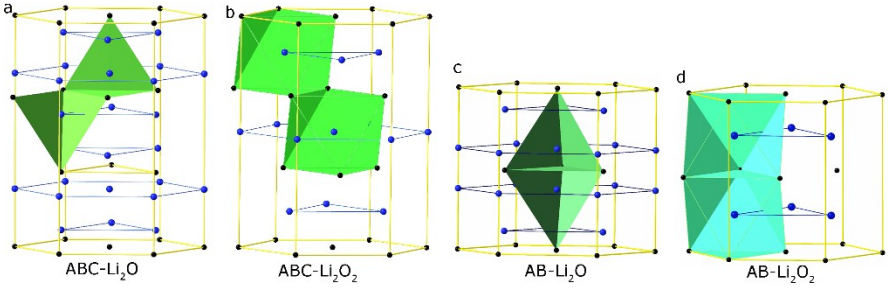

Figure S1 Prototypes of Li_2O_2 and Li_2O.

II. Madelung constant matrix

Of the $P4_2/nmc$ unit cell with two formula Li_6CoO_4, the Madelung constant matrix is:

−0.80	−0.01	−0.21	0.00	−0.10	−0.15	−0.10	−0.15	−0.15	−0.10	−0.15
	−0.80	0.00	−0.21	−0.15	−0.10	−0.15	−0.10	−0.10	−0.15	−0.10
		−0.80	−0.01	−0.15	−0.10	−0.15	−0.10	−0.10	−0.15	−0.10
			−0.80	−0.10	−0.15	−0.10	−0.15	−0.15	−0.10	−0.15
				−0.76	−0.19	0.00	−0.01	−0.17	−0.13	−0.17
					−0.76	−0.01	0.00	−0.13	−0.17	−0.13
						−0.76	−0.19	−0.17	−0.13	−0.17
							−0.76	−0.13	−0.17	−0.13

−0.76	−0.19	0.00
	−0.76	−0.01
		−0.76

The matrix is lower-upper symmetric and only the upper elements are shown.

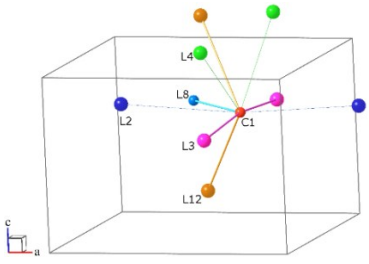

Figure S2 Neighbor connection of Co ion (C1) to Li ions (L2-4, 8, 12). Two L3-O_4 sharing corner with C1-O_4 for the periodicity along **a** axis, L1-O_4 along **b** axis and L10-O_4 along **c** axis; while one L6-O_4 sharing edge with C1-O_4.

Table S1 More details for Table I in the text. Letters "L" and "C" represent Li and Co. The values of Madelung matrix elements are all negative. Bond length r_{ij} and Madelung matrix element M_{ij} are in unit of Å and $Å^{-1}$,

respectively.

Sharing Pattern		pair	r_{ij}	$\|M_{ij}\|$
Co-Li	Edge	C1,L(5,7,8,10); C2,L(6,9,11,12)	2.59	0.12
	Corner	C1,L(6,9,11,12);C2,L(5,7,8,10)	3.05	0.13
		C1,L(2,3); C2,L(1,4)	3.26	0.15
		C1,L(1,4);C2,L(2,3)	3.88	0.17
Li_{4d}-Li	Edge	L1,2; L3,4	2.31	0.21
		L1,L(6,9,11,12); L2,L(5,7,8,10); L3,L(5,7,8,10); L4,L(6,9,11,12)	2.33	0.1
	Corner	L1,L(5,7,8,10); L2,L(6,9,11,12); L3,L(6,9,11,12); L4,L(5,7,8,10)	3.13	0.15
Li_{8f}-Li_{8f}	Edge	L5,9; L6,10; L7,11; L8,12	2.38	0.19
	Corner	L5,L(8,10); L6,L(9,11); L7,L(8,10); L12,L(9,11);	2.83	0.13
		L5,L(6,12); L7,L(6,12); L8,L(9,11); L10,L(9,11)	4	0.17

III. Energy landscapes for Li/vacancy distribution configurations of delithiated phases

Nine distinct configurations are obtained for Li_5CoO_4 and $LiCoO_4$ filtered among $C_{12}^2 = 66$ configurations generated by combination algorithm, thirty-one for Li_4CoO_4 and Li_2CoO_4 filtered among $C_{12}^4 = 495$ configurations, and fifty-one for Li_3CoO_4 among $C_{12}^6 = 924$ configurations. Different from cluster-expansion method, here repeating configurations are filtered and first-principles calculations are performed for all distinct configurations. Notably, the total energy landscapes show energy fluctuation not small, seen in Figure S3, suggesting the effect of Li/vacancy distribution on the phases is not ignorable.

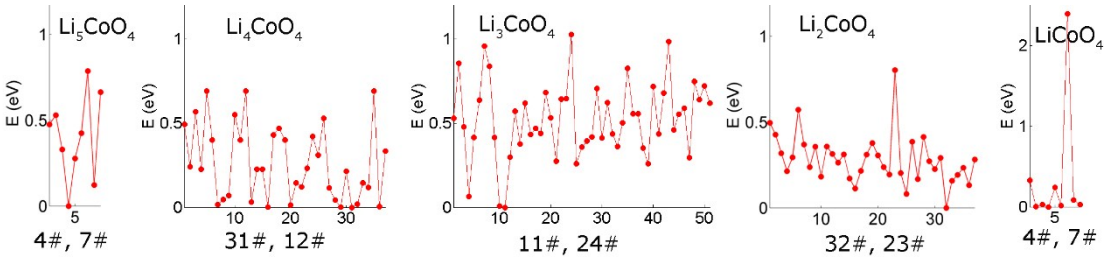

Figure S3 Calculated total energy landscapes for assumed delithiated phases. The unit of energy difference is eV/f.u. The horizontal axis is serial numbers, increasing with Madelung energies, and the serial number of the most stable and instable configurations are labeled below.

IV. Electrochemical Performance

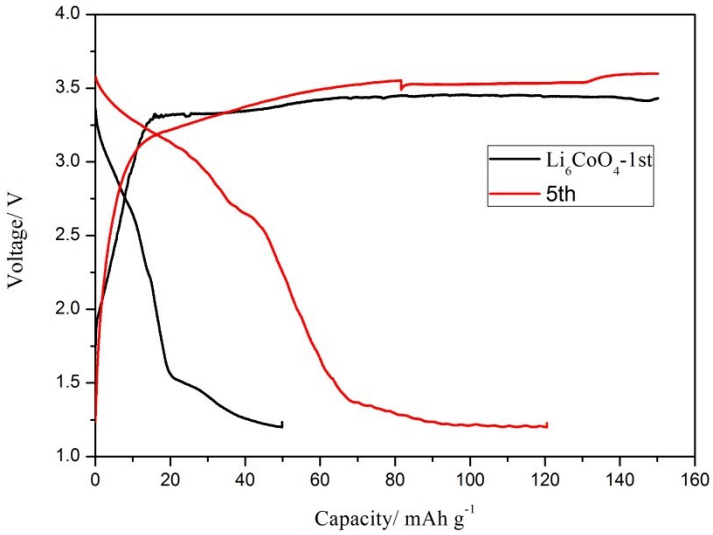

Figure S4 The first (black) and fifth (red) charge and discharge curves of Li/Li_6CoO_4 cell.

Reference

1. Chen, Z.; Li, J., A new method applicable to study solid compounds with multiple polyhedral structures. *Journal of Computational Chemistry* **2016,** *37* (16), 1476-1483.