

Supplementary information for: The Intriguing Question of Anionic Redox in High-Energy Density Cathodes for Li-ion Batteries

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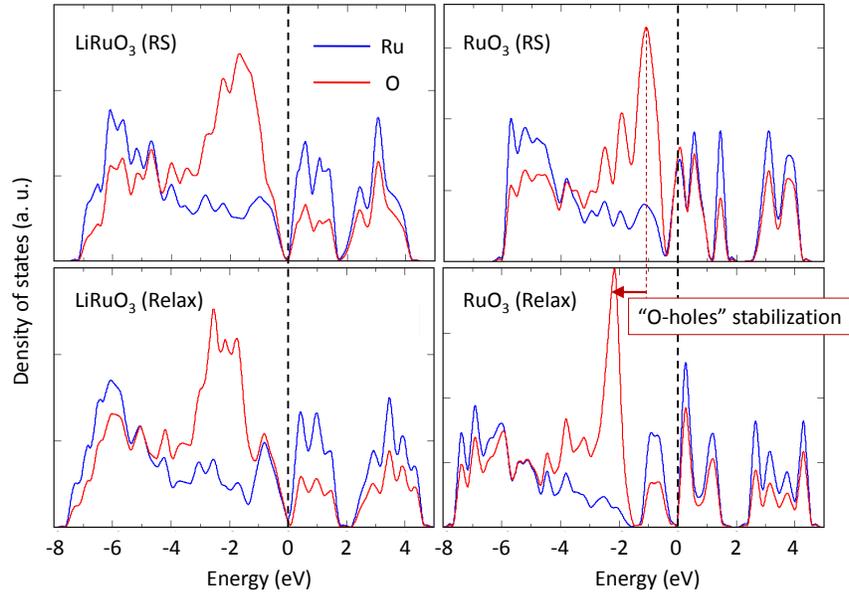


Fig. SI1 Density of states (DOS) of the LiRuO_3 and RuO_3 structures, as obtained from DFT+U calculations in the rigid structure model (RS) and after full structural relaxation, showing that the O-band is significantly shifted down to lower energy at RuO_3 compared to the DOS computed within the rigid structure approach, due to the stabilization of the oxygen network through the formation of short O-O dimers.

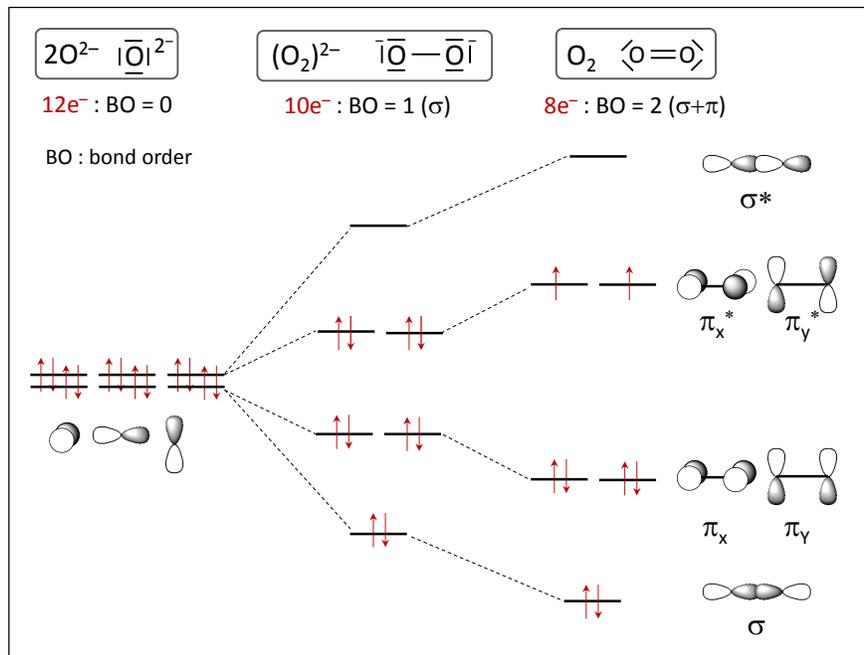


Fig. SI2: Orbital interaction diagram for the formation of the $(O_2)^{2-}$ peroxide and O_2 gas from the progressive oxidation of two non interacting O^{2-} anions. The shortening of the O-O distance leads to the splitting of the O^{2-} ($2p$)-orbitals into two σ - and four π -type molecular orbitals. The number of electrons for each species is indicated in red in addition to the total bond order. Bond orders correspond to $\frac{1}{2}(N_e^B - N_e^{AB})$ where N_e and N_e^{AB} refer to the number of bonding and antibonding electrons, respectively.

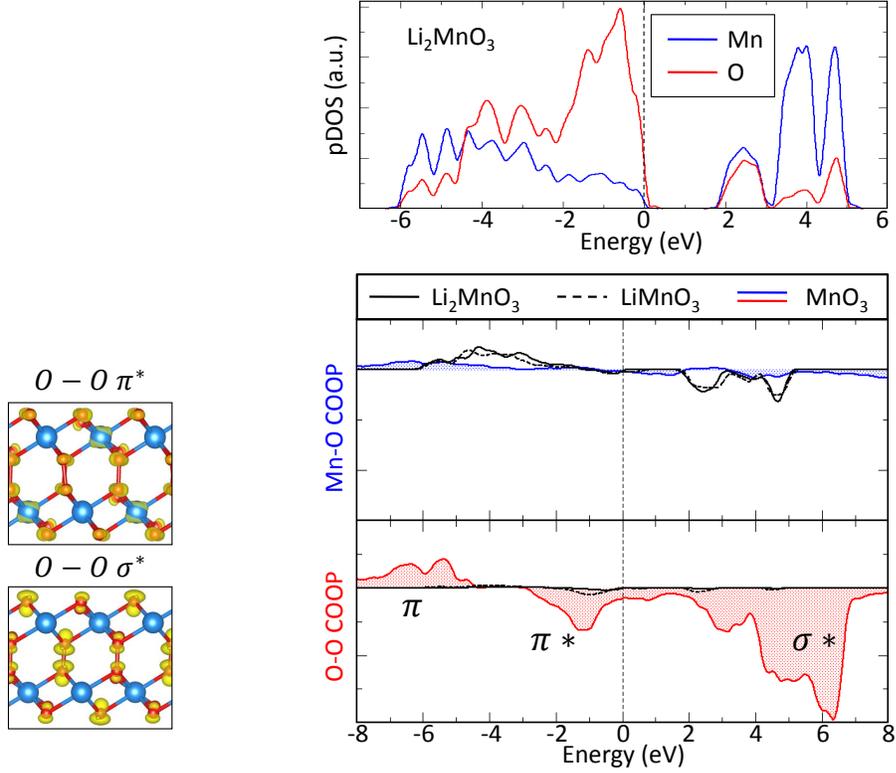


Fig. SI3: Density of States (DOS) of the fully relaxed Li_2MnO_3 structure showing the predominant contribution of the oxygen levels at the Fermi level and Crystal Orbital Overlap populations (COOP) computed for the Mn-O and O-O bonds in the fully relaxed $\text{Li}_{2-x}\text{MnO}_3$ phases at $x = 0, 1$ and 2 . The formation of strongly oxidized O-O dimers is identified at $x = 2$ by the emptying of all the σ^* and part of the π^* O-O electronic levels which corresponds to $(\text{O}_2)^{n-}$ with $n \leq 2$ from the O_2 molecular diagram of Figure SI2. The negligible Mn-O COOPs obtained for MnO_3 compared to LiMnO_3 and Li_2MnO_3 is compatible with the decrease of Mn-O bond covalency upon delithiation and agrees with the O-O dimer decoordination from the metallic network when 2Li are removed. The orbitals associated with the emptied σ^* and π^* electronic levels are represented on the left part of the Figure.

Table S1: Computed averaged Bader atomic net populations in $\text{Li}_{2-x}\text{MO}_3$ ($\text{M} = \text{Ru}, \text{Mn}$) as a function of the Lithium content $x = 0, 1, 2$. The values in parenthesis give the percentage of electron loss per atom in the rigid band model RB (removal of electrons) and in the fully relaxed $\text{Li}_{2-x}\text{MO}_3$ structures (Relaxed).

		RB		Relaxed	
$\text{Li}_{2-x}\text{MO}_3$	x	M	O	M	O
M = Ru($4d$)	0	6.53	7.06	6.53	7.06
	1	6.19 (37%)	6.86 (21%)	6.15 (46%)	6.91 (18%)
	2	5.90 (25%)	6.64 (25%)	6.08 (7%)	6.63 (31%)
M = Mn($3d$)	0	5.26	7.15	5.26	7.15
	1	5.15 (10%)	6.86 (30%)	5.22 (4%)	6.88 (32%)
	2	5.10 (13%)	6.59 (29%)	5.38 (-17%)	6.54 (39%)

The results listed in the table show the cumulative cationic and anionic oxidation of $\text{Li}_{2-x}\text{RuO}_3$ from $x = 0$ to 1 and $x = 1$ to 2, respectively. The removal of 1Li shows a greater oxidation of Ru compared to O while the second Li-removal shows a greater oxidation of O. The comparison between the RB and fully relaxed results for $\text{Li}_{2-x}\text{RuO}_3$ clearly shows that a $\text{M} \rightarrow \text{O}$ charge transfer occurs when the LiRuO_3 structure is relaxed (greater oxidation of Ru after structural relaxation) while a $\text{O} \rightarrow \text{M}$ charge transfer occurs when the RuO_3 structure is relaxed (greater oxidation of O after structural relaxation). This highlights the partial reduction of the transition metal when the reductive coupling mechanism takes place. For the $\text{Li}_{2-x}\text{MnO}_3$ electrode, the removal of two consecutive Li confirms the predominant anionic redox: the oxidation of O is much larger than for the Ru-based material whatever is x and systematically increased after structural relaxation, in agreement with the lack of $\text{Mn}(3d)/\text{O}(2p)$ overlap. The MnO_3 phase associated with the formation of strongly oxidized $(\text{O}_2)^{n-}$ (Relaxed) clearly shows the reduction of the Mn ions (negative charge transfer). Note that the Mn Bader net population obtained for MnO_3 (5.38) is very close to that obtained in the layered LiMnO_2 phase (5.45) in which Mn oxidation state is +3.