Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Suppressing initial capacity fade in Li-rich Li_5FeO_4 with anionic redox by partial Co substitution – a first-principles study

Anu Maria Augustine,[ab] Vishnu Sudarsanan,[ab] and P. Ravindran*[ab]

[a] Department of Physics, Central University of Tamil Nadu, Thiruvarur-610005, India;

[b] Simulation Center for Atomic and Nanoscale MATerials, Central University of Tamil Nadu, Thiruvarur, Tamil Nadu, 610005, India.

E-mail: raviphy@cutn.ac.in

Supplementary Information

Table S1

Compound	structural parameters				magnetic moment		
	a (Å)	b (Å)	c (Å)	V (Å^3)	Fe (μ_B/atom)	Co (μ_B/atom)	Total (μ_B/f.u)
Li_5FeO_4	9.195	9.253	9.244	786.43	4.116		4.796
	9.153[a]	9.218[a]	9.213[a]	777.32[a]			
$Li_{5.125}Fe_{0.875}Co_{0.125}O_4$	9.243	9.244	9.258	791.01	4.117	2.586	4.554
$Li_{5.25}Fe_{0.75}Co_{0.25}O_4$	9.292	9.239	9.268	795.7	4.117	2.586	4.313
$Li_{5.375}Fe_{0.625}Co_{0.375}O_4$	9.332	9.226	9.282	799.19	4.115	2.574	4.072
$Li_{5.5}Fe_{0.5}Co_{0.5}O_4$	9.342	9.265	9.29	804.12	4.121	2.588	3.83
$Li_{5.625}Fe_{0.375}Co_{0.625}O_4$	9.336	9.267	9.316	805.84	4.121	2.588	3.588
$Li_{5.75}Fe_{0.25}Co_{0.75}O_4$	9.331	9.285	9.339	809.13	4.124	2.588	3.348
$Li_{5.875}Fe_{0.125}Co_{0.875}O_4$	9.347	9.263	9.348	809.41	4.134	2.591	3.107
Li_6CoO_4	9.351	9.305	9.361	814.41	2.594	2.866	
$Li_5Fe_{0.875}Co_{0.125}O_4$	9.194	9.248	9.232	784.97	4.116	2.953	4.668
$Li_5Fe_{0.75}Co_{0.25}O_4$	9.196	9.239	9.222	783.51	4.116	2.954	4.54
$Li_5Fe_{0.625}Co_{0.375}O_4$	9.196	9.226	9.209	781.26	4.117	2.952	4.412
$Li_5Fe_{0.5}Co_{0.5}O_4$	9.191	9.219	9.206	780.11	4.116	2.951	4.285
$Li_5Fe_{0.375}Co_{0.625}O_4$	9.192	9.204	9.191	777.57	4.116	2.953	4.156
$Li_5Fe_{0.25}Co_{0.75}O_4$	9.197	9.19	9.179	775.85	4.116	2.953	4.028
$Li_5Fe_{0.125}Co_{0.875}O_4$	9.195	9.178	9.167	773.6	4.116	2.952	3.901
Li_5CoO_4	9.194	9.175	9.153	772.12	2.953	3.773	
$Li_{4.875}Fe_{0.875}Co_{0.125}O_4$	9.174	9.261	9.243	785.23	4.115	3.143	4.777
$Li_{4.75}Fe_{0.75}Co_{0.25}O_4$	9.163	9.275	9.24	785.3	4.113	3.143	4.758
$Li_{4.625}Fe_{0.625}Co_{0.375}O_4$	9.154	9.28	9.236	784.54	4.113	3.145	4.74
$Li_{4.5}Fe_{0.5}Co_{0.5}O_4$	9.125	9.288	9.226	781.88	4.113	3.148	4.722
$Li_{4.375}Fe_{0.375}Co_{0.625}O_4$	9.105	9.291	9.238	781.42	4.114	3.146	4.703
$Li_{4.25}Fe_{0.25}Co_{0.75}O_4$	9.095	9.27	9.258	780.45	4.114	3.146	4.685

$Li_{4.125}Fe_{0.125}Co_{0.875}O_4$	9.124	9.227	9.24	777.85	4.114	3.147	4.668
Li_4CoO_4	9.09	9.31	9.179	776.71	3.15	4.647	

[a] Johnson, C. S., Kang, S. H., Vaughey, J. T., Pol, S. V., Balasubramanian, M., & Thackeray, M. M. (2010). Li2O Removal from Li5FeO4: A cathode precursor for lithium-ion batteries. *Chemistry of Materials*, *22*(3), 1263-1270.

Figure S1

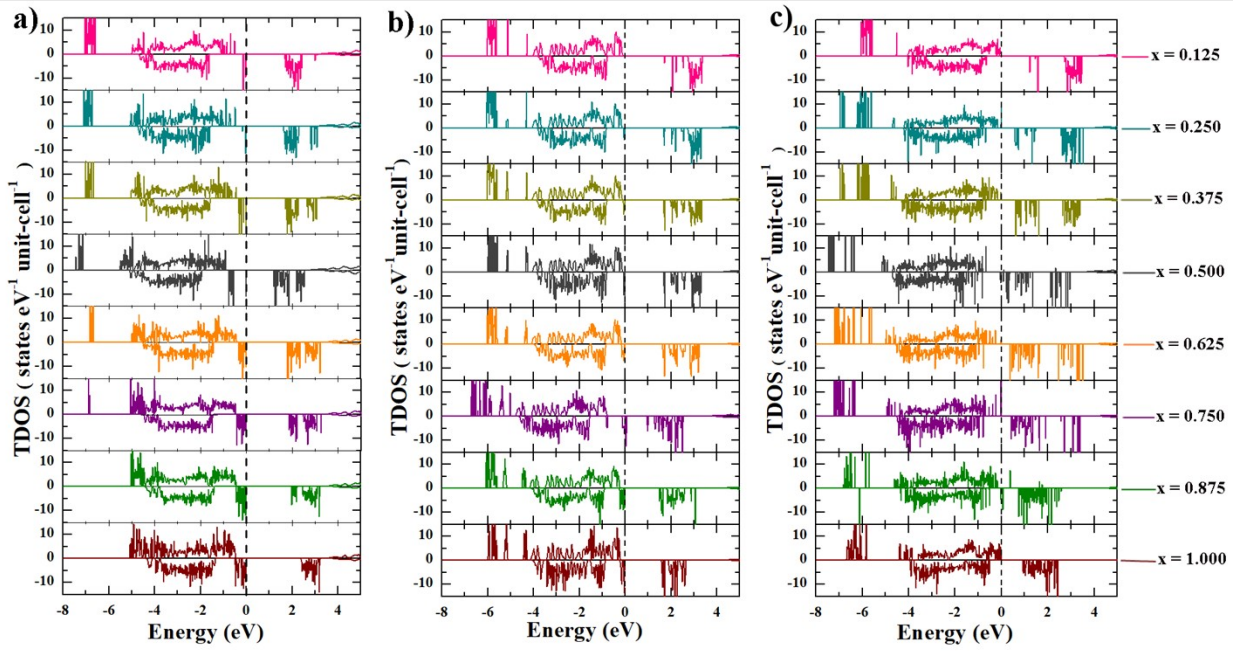

Fig. S1 The calculated total density of states for $Li_yFe_{(1-x)}Co_xO_4$ systems where (a) y = 5+x, (b) y = 5 and (c) y = 5-x ; x = 0.00, 0.125, 0.250, 0.375, 0.500, 0.625, 0.750, 0.875, 1.00 obtained from spin-polarized GGA + *U* calculation.

Supplementary Note S1 : Structural models

As we have discussed in the manuscript, the orthorhombic crystal structure of Li_5FeO_4 can be defined as the substitution of a single Fe^{3+} ion by removing three Li from the 2 x 2 x 2 supercell of rocksalt phase Li_2O. This substitution will introduce 16 Li vacancies in the crystal lattice. In the present study, we have substituted Co at the Fe sites in $Li_yFe_{(1-x)}Co_xO_4$ with x = 0.00, 0.125, 0.250, 0.375, 0.500, 0.625, 0.750, 0.875, 1.00 and y = 5+x, 5, 5-x where Co posses +2, +3, and +4 oxidation states depending upon the composition. To obtain Co^{2+} we have added an extra Li with each Co ion. In this case, the Li will be introduced to the Li vacancy site adjacent to the substituted Co sites (note that there are 16 Li vacant sites already available in each unit cell of Li_5FeO_4). Therefore, when we increase the Co^{2+} concentration, the Li concentration also get increases. The Li and Co site at each Co^{2+}

concentration is given in Figure S2 (a). To model the Co^{3+} substitution, the Li concentration is unaltered since Fe is in +3 oxidation state. The Co^{3+} substituted sites at different Co concentrations are shown in Figure S2 (b). To model Co^{4+} substitution, we have removed one of the Li closer to the substituted Co site. The respective Li and Co position at each stage of Co^{4+} substitutions are given in Figure S2 (c). We have modeled the Co substitution in such a way that the Co ions are distributed homogeneously throughout the system.

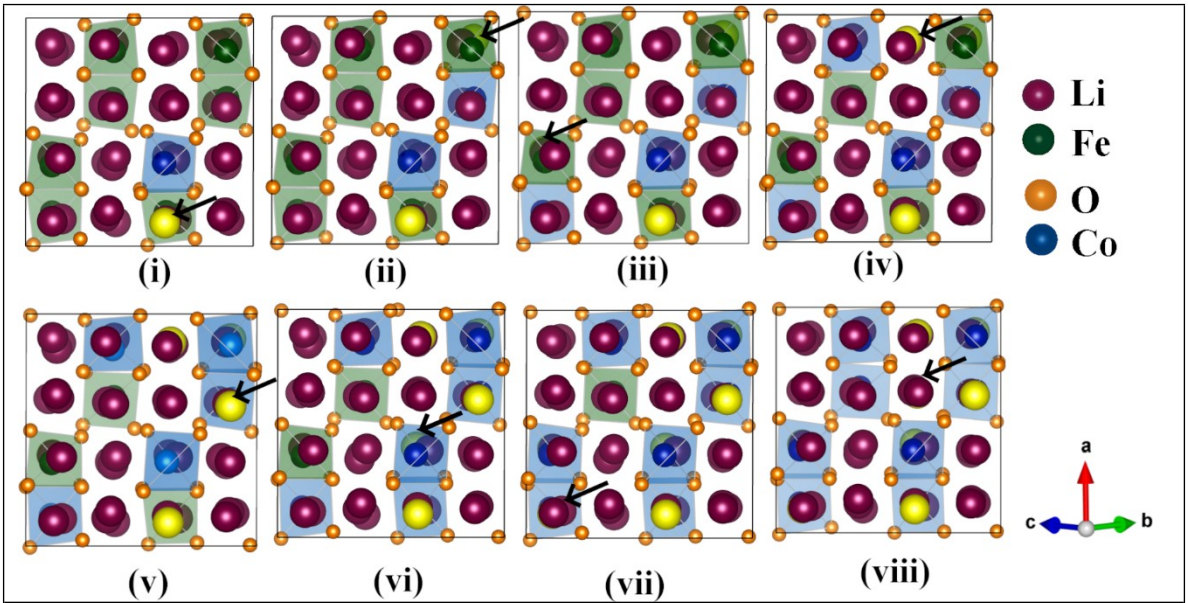

Figure S2 (a): The Co substitution and Li co-substitution to obtain Co^{2+} at different Co concentrations in $Li_yFe_{(1-x)}Co_xO_4$. The yellow balls represent the co-substituted Li (each arrow shows the Li added at a particular composition) with Co^{2+} substitution. The FeO_4 and CoO_4 tetrahedra are given in polyhedral representation. The concentration of Co atom increases from (i) to (viii) (x = (i) 0.125, (ii) 0.250, (iii) 0.375, (iv) 0.500, (v) 0.625, (vi) 0.750, (vii) 0.875, (viii) 1.00)

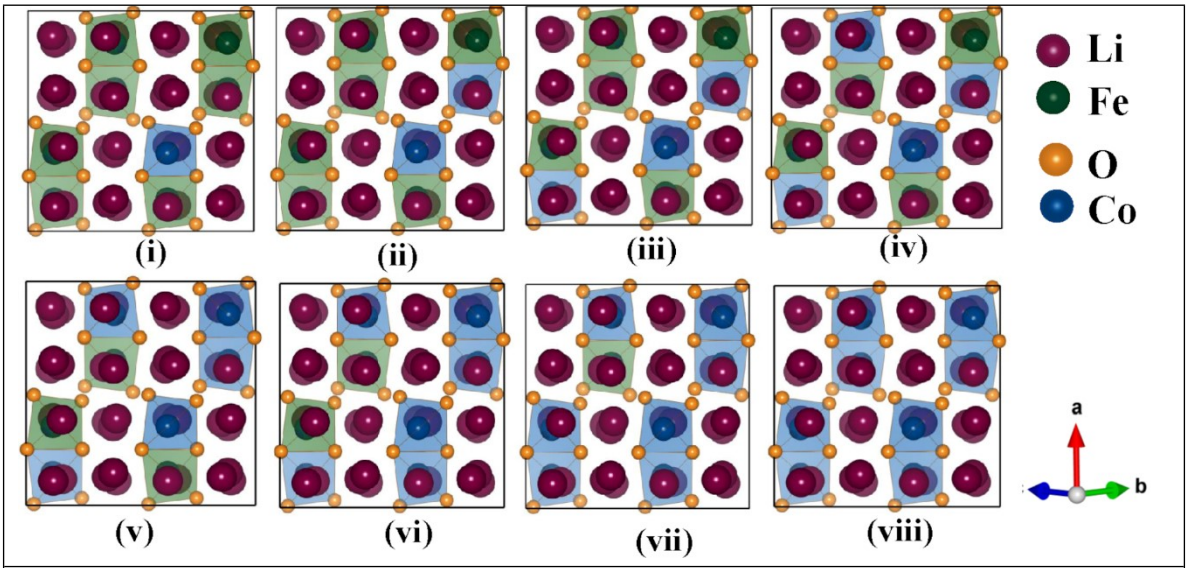

Figure S2 (b): The Co^{3+} substitution at different Co concentrations in $Li_yFe_{(1-x)}Co_xO_4$. The Li concentration did not change since we are replacing Fe having +3 oxidation state with Co. The FeO_4 and CoO_4 tetrahedra are given in polyhedral representation. The concentration of Co atom increases

from (i) to (viii) (x = (i) 0.125, (ii) 0.250, (iii) 0.375, (iv) 0.500, (v) 0.625, (vi) 0.750, (vii) 0.875, (viii) 1.00)

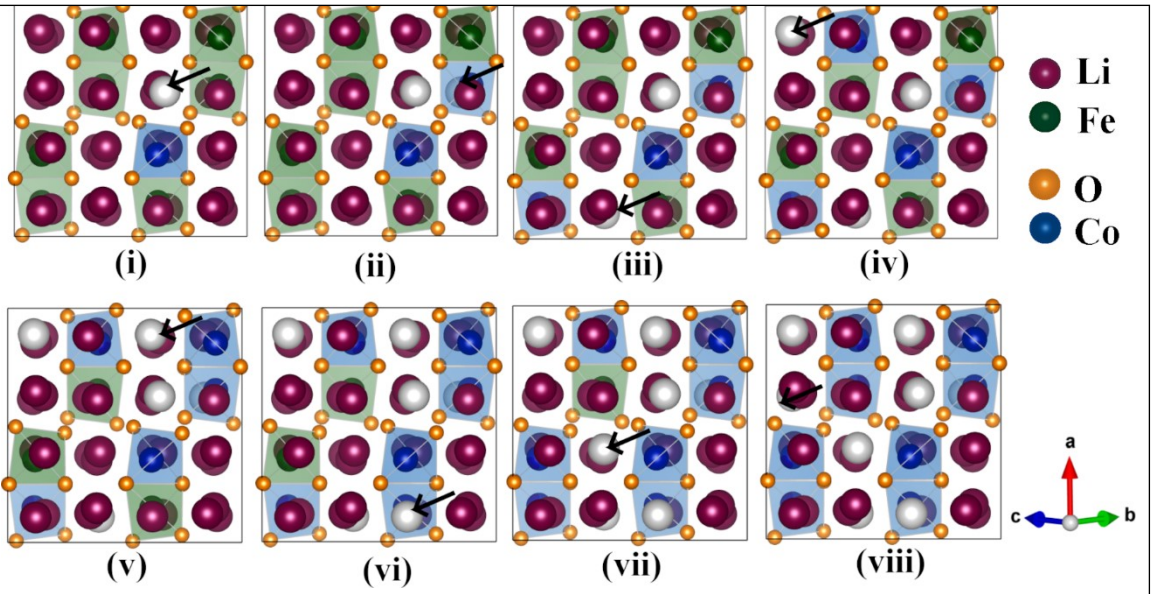

Figure S2 (c): The Co^{4+} substitution and Li removal at different Co concentrations in $Li_yFe_{(1-x)}Co_xO_4$. The gray-colored spheres represented the Li vacancies introduced (each arrow shows the Li vacancy introduced at the particular composition) to model Co^{4+} substitution. The FeO_4 and CoO_4 tetrahedra are given in polyhedral representation. The concentration of Co atom increases from (i) to (viii) (x = (i) 0.125, (ii) 0.250, (iii) 0.375, (iv) 0.500, (v) 0.625, (vi) 0.750, (vii) 0.875, (viii) 1.00)