Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

First Principles Calculations on Lithium Diffusion near Surface and in Bulk of Fe-doped $LiCoPO_4$

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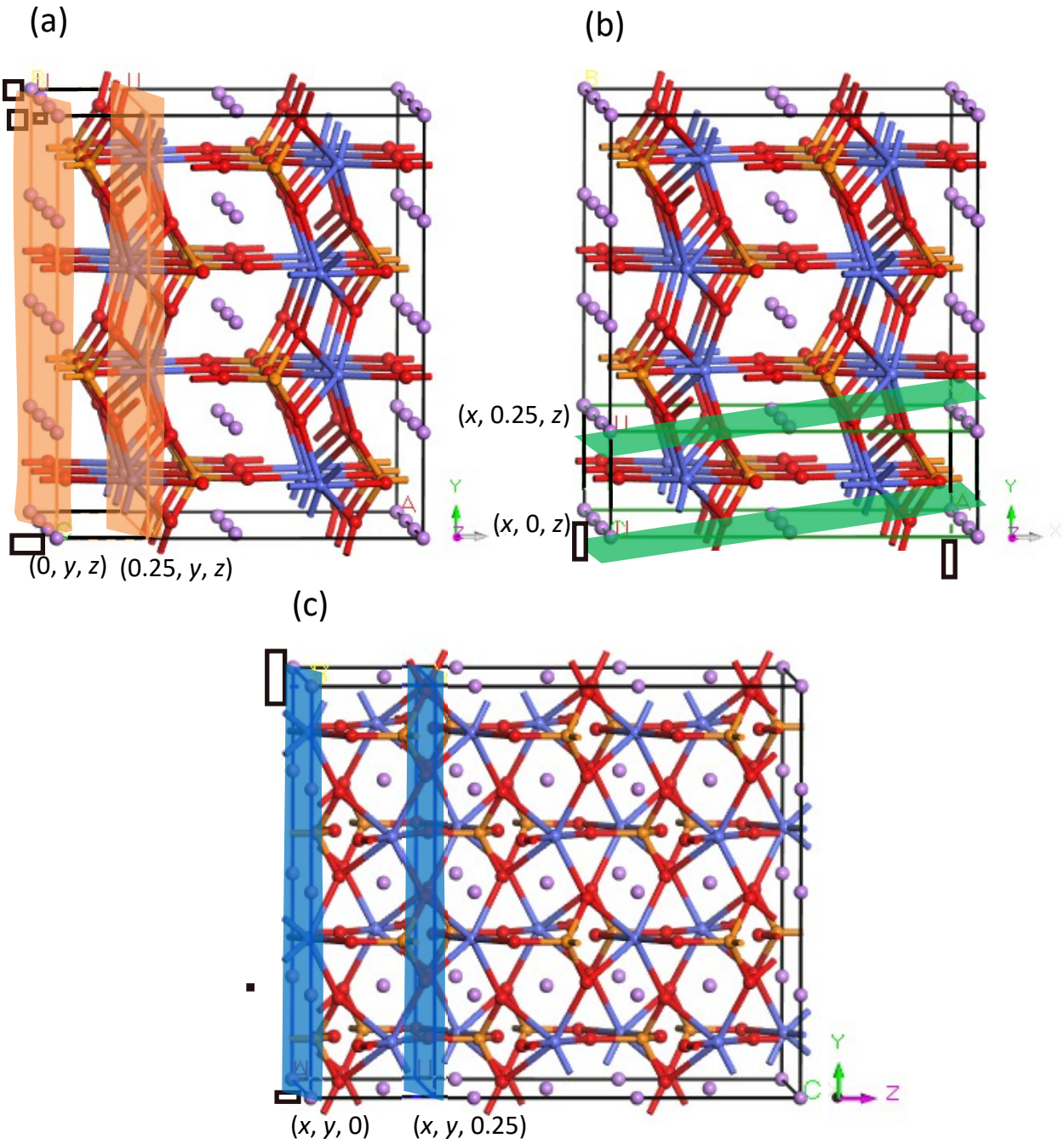

Figure S1. Optimized bulk structure of $LiCoPO_4$ and possible termination planes for (a) (1 0 0), (b) (0 1 0), and (c) (0 0 1) surfaces.

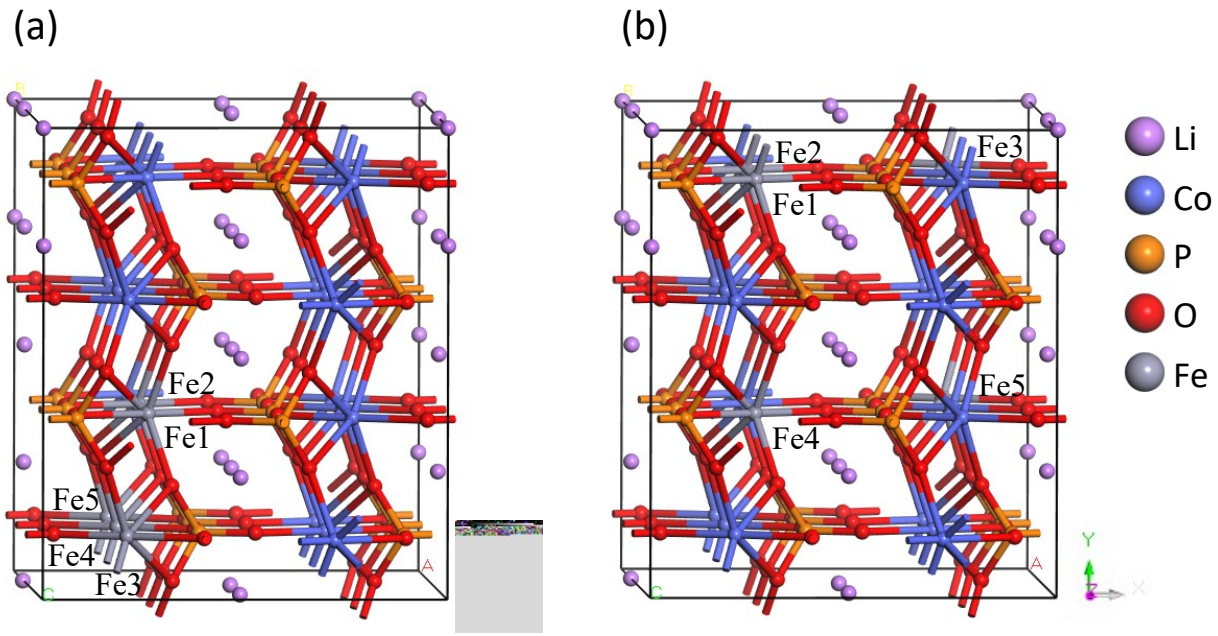

Figure S2. Supercell structure of Fe doped $LiCoPO_4$ after geometry optimization with (a) aggregated and (b) separated distribution of iron atoms.

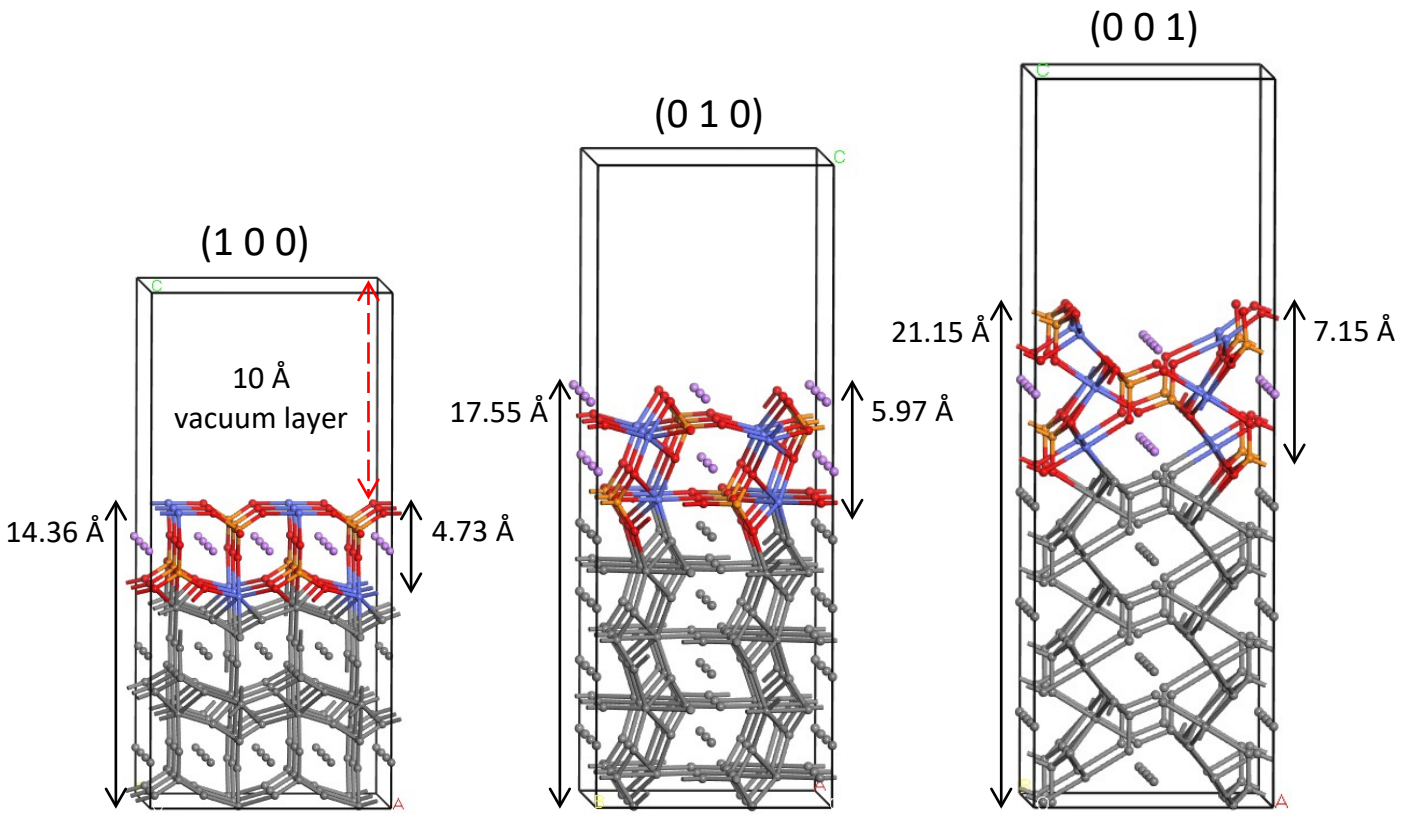

Figure S3. Slab model with layers sufficiently thick for converged surface energy in (1 0 0), (0 1 0) and (0 0 1) orientation. The grey part at the bottom represents fixed atoms in bulk configuration and 10 Å vacuum layer.

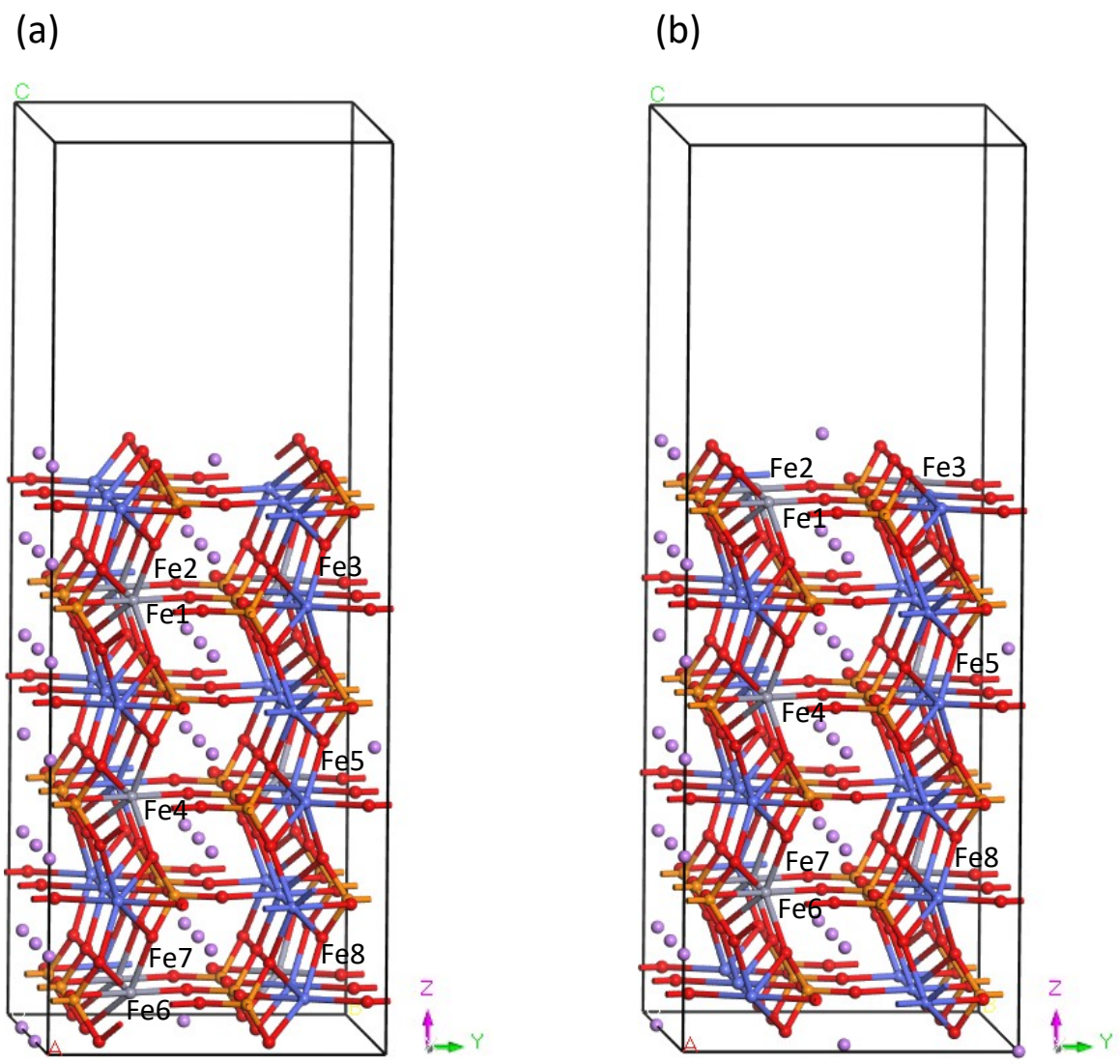

Figure S4. Two types of surface models with the same Fe doping concentration as bulk material.

($Li_{36}Fe_8Co_{28}P_{36}O_{144}$)

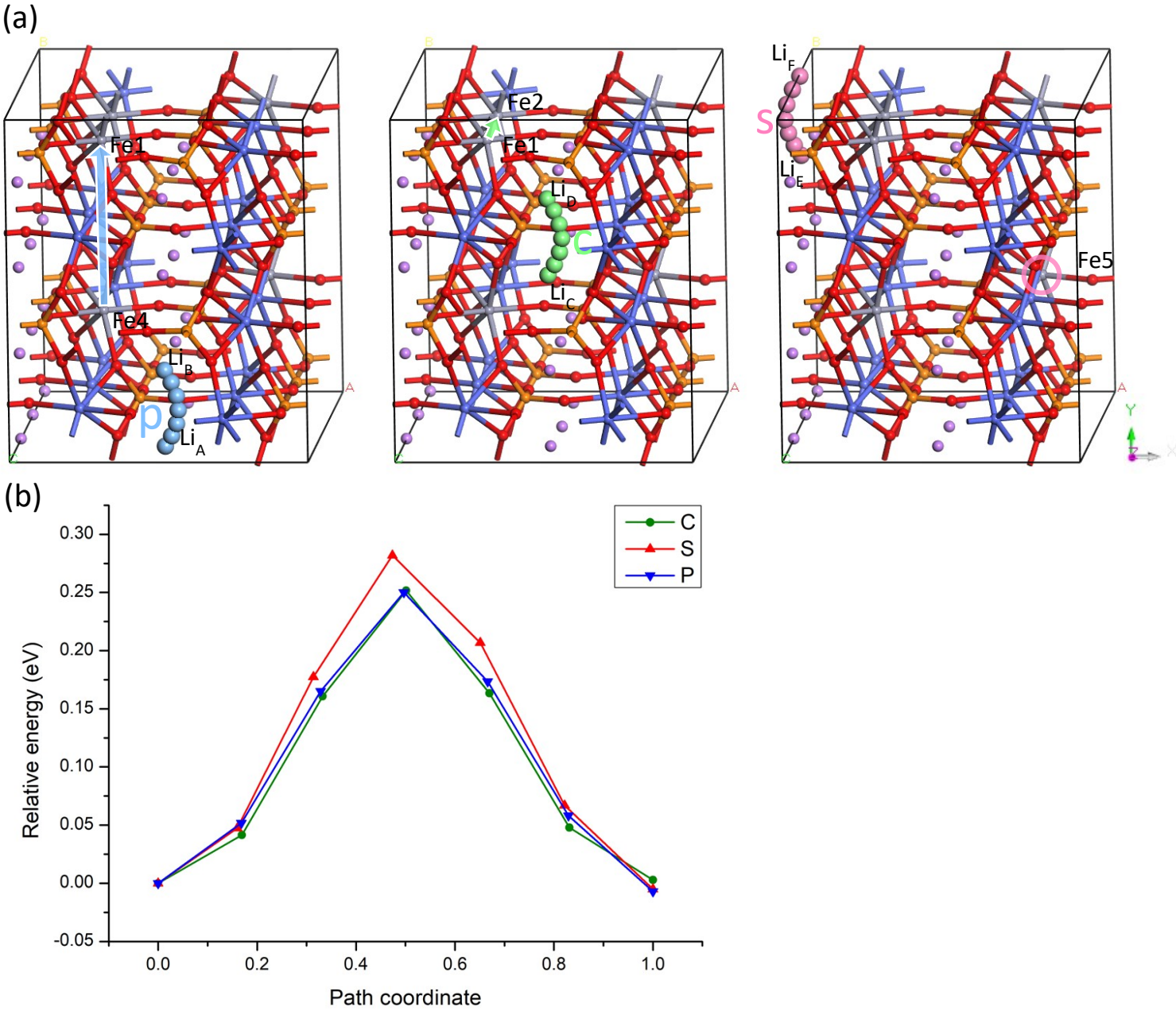

Figure S5. (a) Diffusion pathways of Li ion-polaron complex along the [0 1 0] direction. Blue, green and red spheres illustrate the trajectories of parallel, crossing and single diffusion processes, respectively. Arrows and circle indicate the direction of polaron hopping or stationary location for each EDP. (b) The corresponding activation energies for crossing (C), single (S), and parallel (P) elementary diffusion processes plotted in green, red, and blue, respectively.

Table S1. Energy per atom for systems with different iron distribution.

Distribution	Doped Fe-Fe Average Distance (Å)	Energy/Atom (eV)
Aggregated	5.01	-446.6976936
Separated	7.59	-446.6987315

Table S2. Average bond length and polyhedral volumes of the CoO_6 and FeO_6 octahedral structures at five Fe doping sites.

Bond	Co1-O	Fe1-O	Co2-O	Fe2-O	Co3-O	Fe3-O	Co4-O	Fe4-O	Co5-O	Fe5-O
Average Bond Length (Å)	2.159	2.187	2.143	2.188	2.145	2.185	2.144	2.187	2.144	2.186
Polyhedra Volume ($Å^3$)	12.388	13.064	12.372	13.077	12.414	13.018	12.387	13.022	12.412	13.053
Bond Length Difference (%)		1.305		2.116		1.896		2.006		1.935
Volume Difference (%)		5.461		5.696		4.865		5.119		5.161

Table S3. Energy of the possible termination planes of low index surfaces.

Orientation	Termination Plane	Energy (eV)	Energy/Atom (eV)
[1 0 0]	(0, 0, 0)	-113871.9751	-451.8729
	(0.25, 0, 0)	-113913.6530	-452.0383
[0 1 0]	(0, 0, 0)	-113921.9886	-452.0714
	(0, 0.25, 0)	-113921.9851	-452.0714
[0 0 1]	(0, 0, 0)	-113900.9675	-451.9880
	(0, 0, 0.25)	-113916.0629	-452.0479

Table S4. Calculated results for low index surfaces.

Orientation	Slab Thickness (Å)	Relaxation Layer Thickness (Å)	Surface Energy (J/m^2)
[1 0 0]	14.36	4.73	0.697
[0 1 0]	17.55	5.97	0.689
[0 0 1]	21.15	7.15	1.036