

Supporting Information

The decisive role of electrostatic interactions in transport mode and phase segregation of lithium ions in LiFePO_4

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1. DFT Calculation Details

The spin-polarized calculations under Density Functional Theory (DFT) were performed with the Vienna *ab initio* simulation package (VASP)^{1, 2} using projector-augmented wave (PAW)³ pseudopotentials. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional with generalized gradient approximation (GGA)⁴ was employed and an effective Hubbard-type correction U parameter of $U = 4.3$ eV to describe the strongly correlated nature of the Fe 3d electron.⁵ The plane-wave energy cut-off was set as 520 eV for the expansion of the electronic wave function, and a Gaussian smearing method with an energy broadening of 0.05 eV was used. The Brillouin zones were sampled with a Gamma-centered $5 \times 2 \times 2$ k-point mesh for a $1a \times 2b \times 1c$ supercell and $2 \times 2 \times 2$ k-point mesh for a $3a \times 2b \times 1c$ supercell using an A-type antiferromagnetic configuration⁵. The files of k-point mesh were generated by VASPKIT.⁶ Besides, we performed the climbing-image nudged elastic band (CI-NEB) method⁷ to calculate the activation energy of ion hopping, which is compared with the activation energy obtained by the Hamiltonian model.

2. Supporting Informations

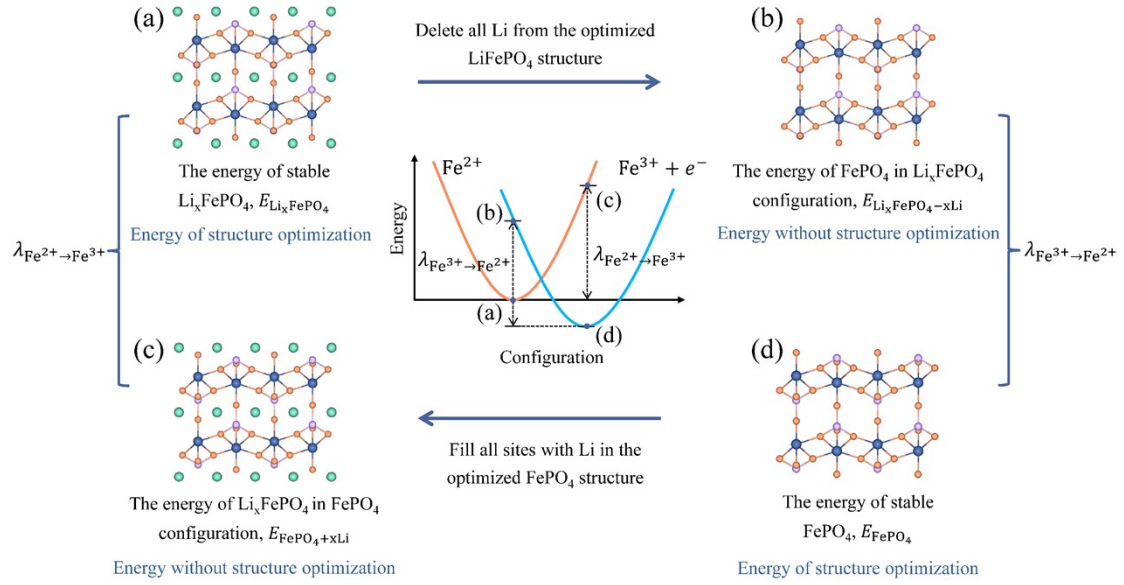


Fig. S1 Schematic diagram for computation of the configuration reorganization energies of coupled ion-electron transfer in LiFePO_4 .

The supercell calculated in DFT method contains several units of LiFePO_4 . E_{LiFePO_4} is the energy of the unit cell. Thus, $E_{\text{LiFePO}_4} = E_{\text{LiFePO}_4}^{\text{cal}}/n$, where $E_{\text{LiFePO}_4}^{\text{cal}}$ is the calculated energy, and n is the number of unit cells contained in the supercell.

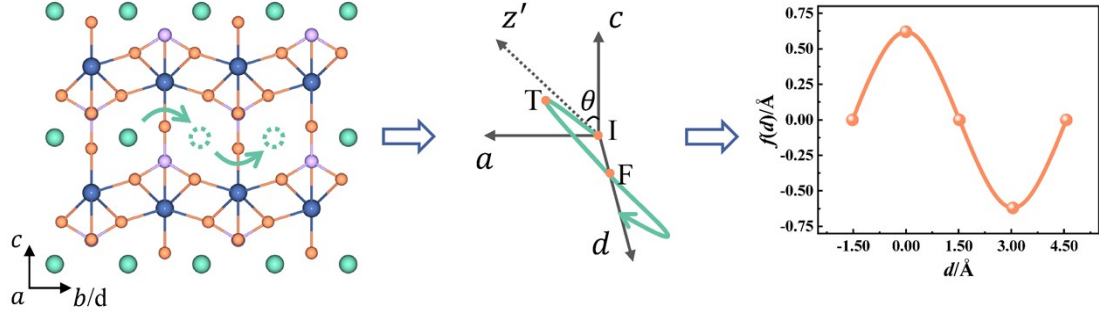


Fig. S2 Schematic illustration of Li^+ transport trajectory and the path function fitted by Fourier series.

By setting up Cartesian coordinates in the lattice, we obtain multiple coordinate matrices M_i including a Li site and six Fe sites adjacent to it,

$$M_i = \begin{bmatrix} \text{Li} \\ \text{Fe}_1 \\ \dots \\ \text{Fe}_{n=6} \end{bmatrix} = \begin{bmatrix} a & d & c \\ a_1 & d_1 & c_1 \\ \dots & \dots & \dots \\ a_{n=6} & d_{n=6} & c_{n=6} \end{bmatrix} \quad (\text{S1})$$

Combining with coordinates of LiO_6 octahedral centers and tetrahedral centers, we fit the path function $f(d)$ by Fourier series in the fourth-dimensional coordinates z' .

$$f(d) = m \cdot \sin(\omega d) + n \cdot \cos(\omega d) + p \quad (\text{S2})$$

The position of Li^+ located at tetrahedral sites is defined as zero coordinates, namely, $d_T = 0 \text{ \AA}$. The values of the parameters are listed in Table S2.

Also, we construct a plane ITF where the Li^+ transport trajectory is located,

$$Aa + Bd + Cc + D = 0 \quad (\text{S3})$$

the values are listed in Table S3. The angle between the plane ITF and c-axis, θ , satisfies

$$\sin \theta = \frac{|C|}{\sqrt{A^2 + B^2 + C^2}} \quad (\text{S4})$$

then

$$a = f(d) \cdot \sin \theta \quad (\text{S5a})$$

$$c = f(d) \cdot \cos \theta \quad (\text{S5b})$$

So far, all parameters of eqn (19) have been obtained.

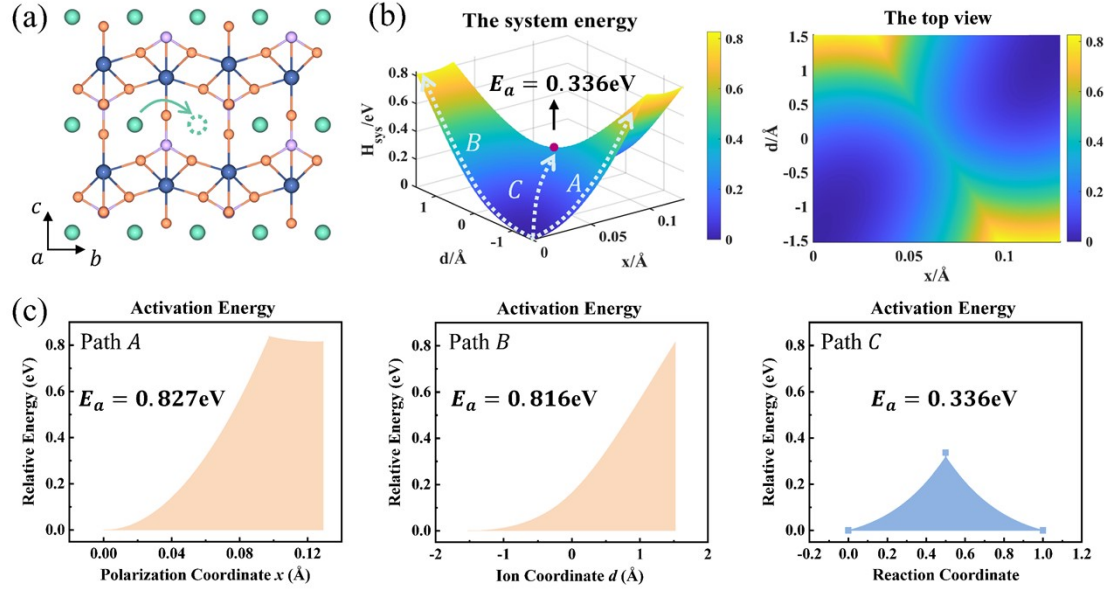


Fig. S3 (a) Structure diagram of Li^+ hopping along the b -axis in LiFePO_4 . (b) Potential energy surface based on the Hamiltonian model (left) and its top view (right) for ion hopping and electron transfer. (c) Potential energy curves of paths A , B , and C .

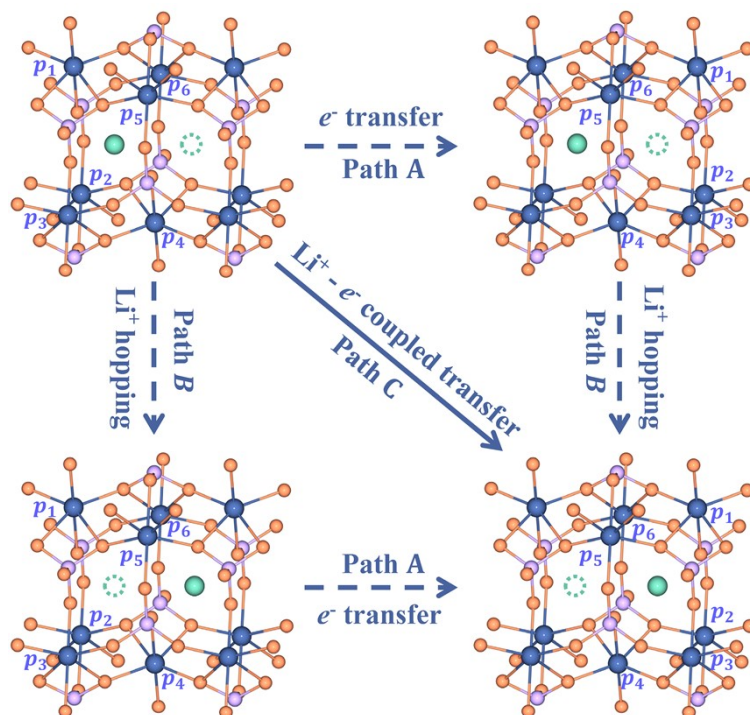


Fig. S4 Schematic illustration of three reaction paths including separate electron transfer, Li^+ hopping, and $\text{Li}^+ - e^-$ coupled transfer.

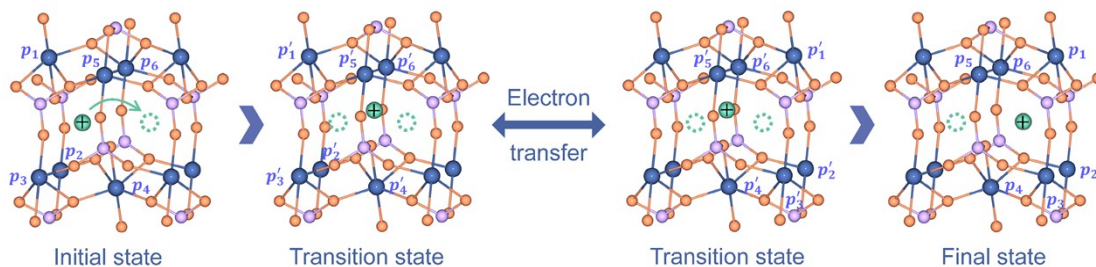


Fig. S5 Schematic illustration of ion-electron coupled transfer process.

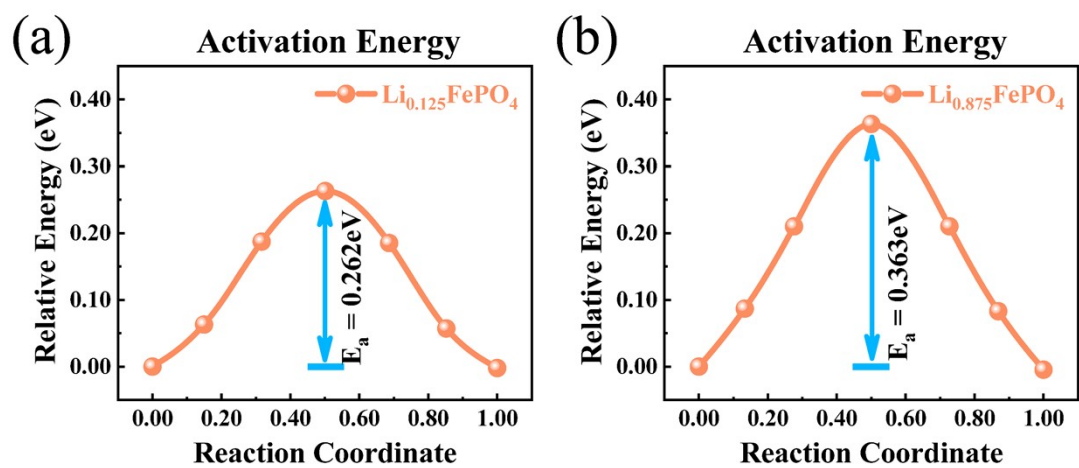


Fig. S6 The activation energy calculated by NEB for Li^+ hopping in (a) $\text{Li}_{0.125}\text{FePO}_4$ and (b) $\text{Li}_{0.875}\text{FePO}_4$.

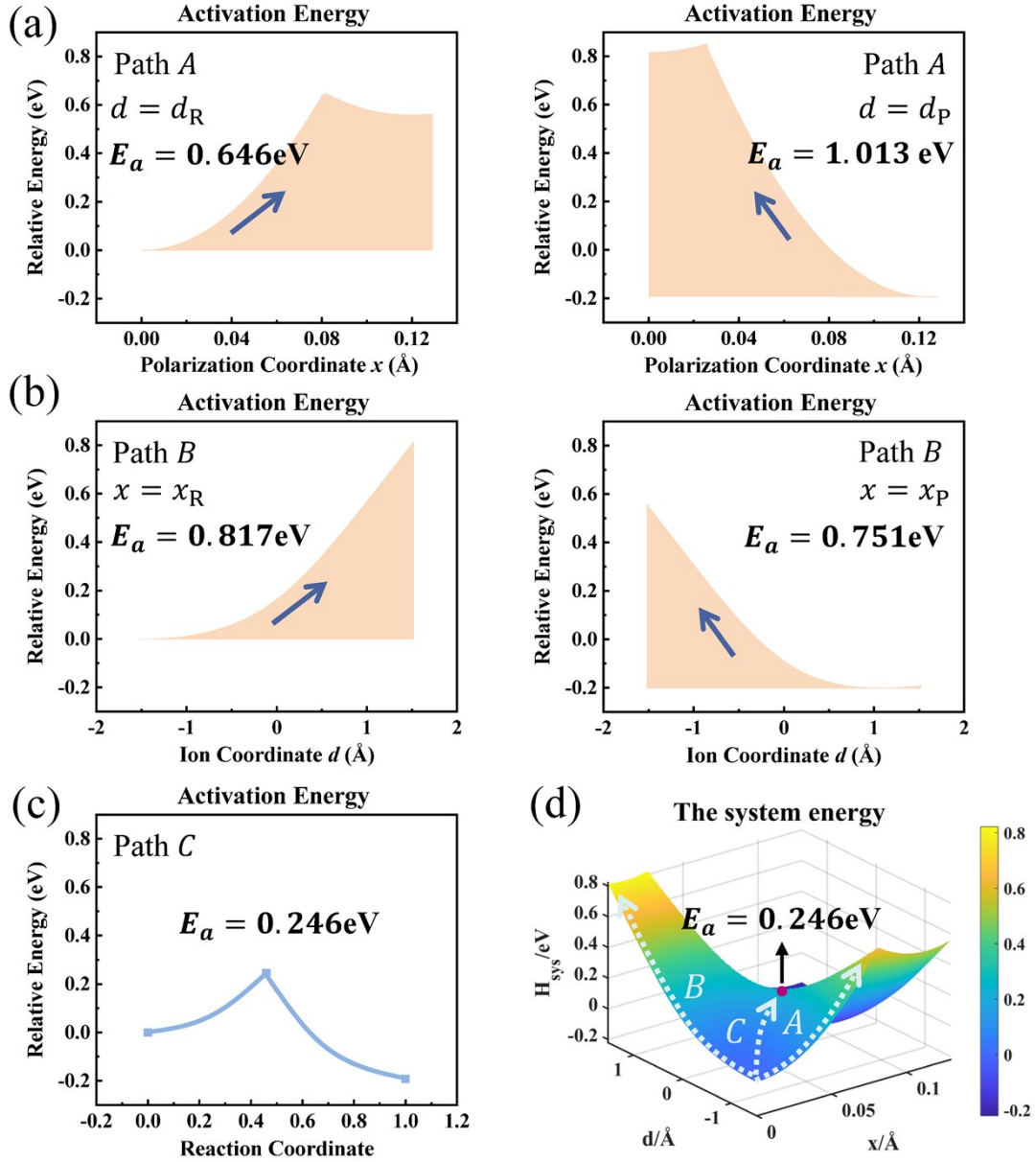


Fig. S7 Potential energy curves for (a) path A of electron transfer, (b) path B of ion hopping, and (c) path C of ion-electron coupled transfer. (d) Potential energy surface for ion-electron coupled transfer in $\text{Li}_{0.125}\text{FePO}_4$ of $3a \times 2b \times 1c$ supercell.

Table S1 The values of model parameters

Category	Item	Value
constant	vacuum permittivity, ϵ_0	$8.85419 \times 10^{-12} \text{ F m}^{-1}$
	elementary charge, e	$1.60219 \times 10^{-19} \text{ C}$
	Boltzmann constant, k_B	$1.380649 \times 10^{-23} \text{ J K}^{-1}$
	temperature, T	298.15 K
polarization	x_R	0 Å
coordinate x	x_P	0.13 Å ^{8,9}

Table S2 The parameters of the path function

Item	ω	m	n	p
Value	1.032	-2.970×10^{-6}	0.620	-9.138×10^{-7}

Table S3 The parameters of the ITF plane

Item	A	B	C	D
Value	1.644	0	-1	0

Table S4 The value of partial charges in $\text{Li}_{0.125}\text{FePO}_4$ of $3a \times 2b \times 1c$ supercell

Category	Item	r_n	α_n	Partial charge
the initial state	q_1	3.317	1.2	0.212
	q_2	3.548	1.0	0.165
	q_3	3.702	1.0	0.158
	q_4	3.317	0.8	0.141
	q_5	3.548	1.0	0.165
	q_6	3.702	1.0	0.158
the final state	q_1	3.317	1.0	0.177
	q_2	3.548	0.8	0.132
	q_3	3.702	1.2	0.190
	q_4	3.317	1.0	0.177
	q_5	3.548	1.2	0.198
	q_6	3.702	0.8	0.126

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