

Supplementary Information for

Unblocking “pinned” Li⁺ ions in novel KTiOPO₄-structured LiVPO₄F enables superior energy storage performance

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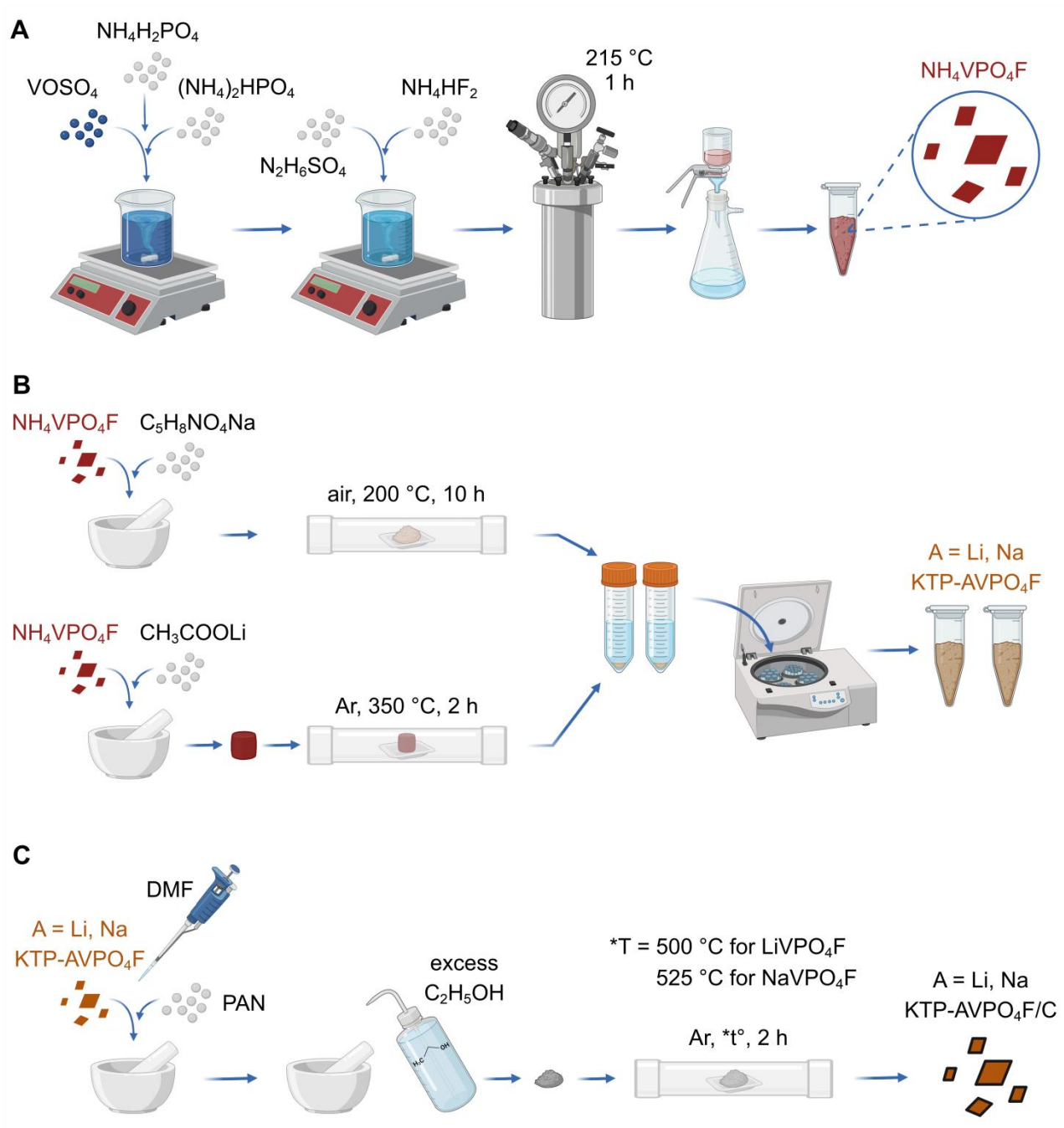


Figure S1. Synthesis schemes for (A) $\text{NH}_4\text{VPO}_4\text{F}$, (B) $\text{KTP-LiVPO}_4\text{F}$ and $\text{KTP-NaVPO}_4\text{F}$, (C) carbon-coated $\text{KTP-LiVPO}_4\text{F}$ and $\text{KTP-NaVPO}_4\text{F}$ ($\text{KTP-AVPO}_4\text{F/C}$ ($\text{A} = \text{Li, Na}$)). Created with BioRender.com

Table S1. Atomic coordinates¹, occupancy factors and U_{iso} values for NH₄VPO₄F.

Atom	Wyckoff	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U _{iso} , Å ²	Occupancy
N1	8 <i>e</i>	0.146(1)	0.652(1)	0.055(2)	0.077(5)	1
H1	8 <i>e</i>	0.107(5)	0.695(8)	−0.075(9)	0.077(5)	1
H2	8 <i>e</i>	0.146(9)	0.549(2)	0.038(14)	0.077(5)	1
H3	8 <i>e</i>	0.107(5)	0.677(9)	0.197(7)	0.077(5)	1
H4	8 <i>e</i>	0.226(3)	0.686(11)	0.062(10)	0.077(5)	1
V1	4 <i>d</i>	0.1338(3)	0.25	0.75	0.011(1)	1
V2	4 <i>a</i>	0	0	0	0.009(1)	1
P1	4 <i>d</i>	0.0687(4)	0.25	0.25	0.005(1)	1
P2	4 <i>c</i>	0.25	0	−0.0769(7)	0.004(14)	1
O1	8 <i>e</i>	−0.0011(7)	0.1362(9)	0.206(1)	0.002(1)	1
O2	8 <i>e</i>	0.1523(5)	0.022(1)	0.051(1)	0.002(1)	1
O3	8 <i>e</i>	0.1393(8)	0.220(1)	0.433(1)	0.002(1)	1
O4	8 <i>e</i>	0.2300(6)	0.1124(9)	−0.222(1)	0.002(1)	1
F1	8 <i>e</i>	−0.0251(5)	0.8733(8)	0.217(1)	0.008(3)	1

¹The positions of the nitrogen and hydrogen atoms (NH₄⁺ cation) were refined using a rigid body: the N-H bond length was fixed (0.95 Å) [37].

Table S2. TEM-EDX data of V:P ratio in KTP-LiVPO₄F.

Area	Atomic Fractions, %	
	V	P
1	49.54	50.46
2	50.33	49.67
3	49.42	50.58
4	50.56	49.44
5	51.99	48.01
6	49.60	50.40
7	50.81	49.19
Average	50.32	49.68
Atomic Errors, %	2.75	2.75

Table S3. TEM-EDX data of O:F ratio in KTP-LiVPO₄F.

Area	Atomic Fractions, %	
	O	F
1	76.88	23.12
2	79.30	20.70
3	79.66	20.34
4	76.96	23.04
5	79.60	20.40
6	81.24	18.76
7	81.76	18.24
8	82.46	17.54
Average	79.73	20.27
Atomic Errors, %	6.20	6.20

Table S4. Atomic coordinates, occupancy factors and U_{iso} values for KTP-LiVPO₄F.²

Atom	Wyckoff	x/a	y/b	z/c	Occupancy
Li1	4a	0.381(1)	0.51(4)	0.76(3)	1
Li2	4a	0.782(23)	0.27(5)	−0.02(6)	0.5
Li3	4a	0.475(18)	0.99(4)	0.39(4)	0.5
V1	4a	0.7501(21)	0.740(4)	0	1
V2	4a	0.8863(11)	0.012(4)	0.249(7)	1
P1	4a	0.8136(14)	0.519(6)	0.256(7)	1
P2	4a	0.998(3)	0.820(3)	−0.007(8)	1
O1	4a	0.892(4)	0.344(7)	0.230(1)	1
O2	4a	0.741(6)	0.471(13)	0.372(12)	1
O3	4a	0.748(6)	0.547(12)	0.135(12)	1
O4	4a	0.872(4)	0.732(9)	0.281(9)	1
O5	4a	0.015(4)	0.941(8)	−0.133(9)	1
O6	4a	0.891(4)	0.718(8)	−0.016(1)	1
O7	4a	0.008(8)	0.985(9)	0.101(8)	1
O8	4a	0.086(3)	0.657(9)	0.017(1)	1
F1	4a	0.733(4)	0.494(11)	−0.133(8)	1
F2	4a	0.747(4)	0.993(9)	0.098(7)	1

²Atomic displacement parameters were fixed to 0.01.

Table S5. Selected interatomic distances for KTP-LiVPO₄F.³

Bond	Distance, Å	Bond	Distance, Å
V1-O2	1.99(1)	V2-O1	2.12(1)
V1-O3	1.87(1)	V2-O4	1.82(1)
V1-O6	1.84(1)	V2-O5	1.82(1)
V1-O8	2.22(1)	V2-O7	2.22(1)
V1-F1	2.09(1)	V2-F1	2.00(1)
V1-F2	1.90(1)	V2-F2	2.25(1)
P1-O1	1.53(2)	P1-O2	1.56(2)
P1-O3	1.55(2)	P1-O4	1.56(2)
P2-O5	1.52(2)	P2-O6	1.55(2)
P2-O7	1.55(1)	P2-O8	1.54(1)

³Semi-rigid body restraints were used to the phosphate groups, allowing the P–O distances to vary in the 1.54±0.02 Å range. The total occupancy for all Li sites was fixed according to the chemical formula. Selected bond lengths for Li sites are summarized in the section (DFT calculations) below.

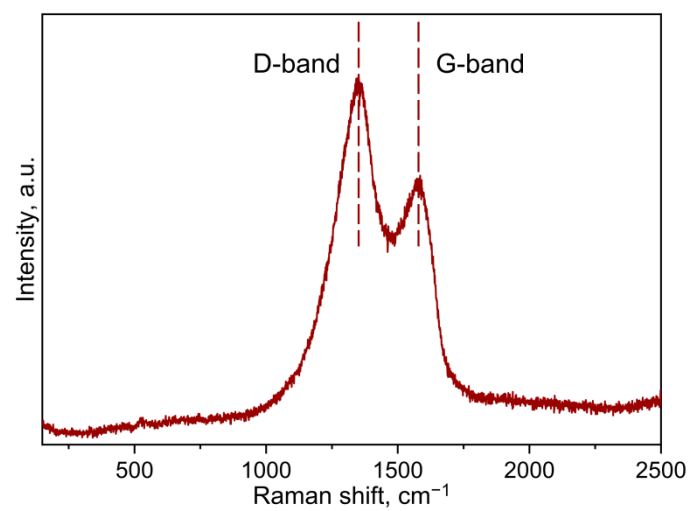


Figure S2. Raman spectra of KTP-LiVPO₄F/C composite material.

Supplementary note 1. DFT benchmarks.

To ensure the accuracy of our computational setup for the nudged elastic band (NEB) method in reproducing migration pathways and energy profiles for Li^+ ions, we initially conducted tests on the ordered bulk KTP-LiVPO₄F structure proposed by H. Kim *et al.* [1], who generously provided it us, enabling one-to-one comparisons. The calculated energy profiles and activation barriers are in a perfect agreement, as shown in Figure S3, which validates the choice of our setup. Our computational setup was $E_{\text{cut}} = 400$ eV and $2 \times 4 \times 2$ k -point mesh; whereas Kim used $E_{\text{cut}} = 520$ eV and $2 \times 3 \times 2$ k -point mesh. A minor alteration in shapes of energetic profiles may arise due to variations in the interpolation methods for 3D migration pathways. Nevertheless, these differences are negligible, and the results are highly consistent.

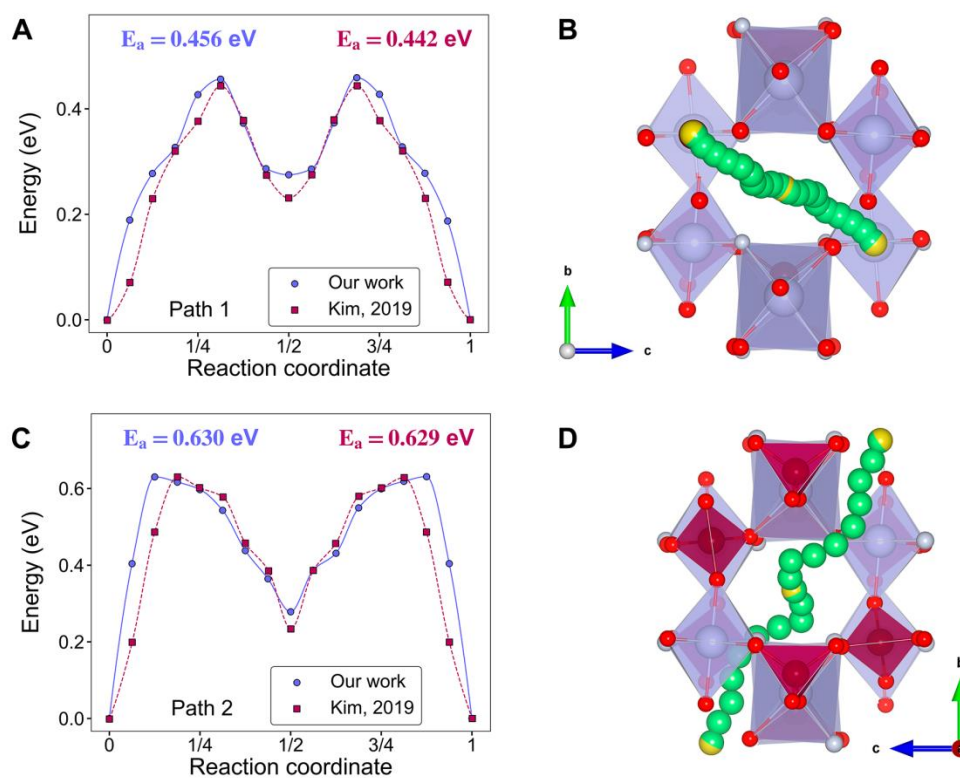


Figure S3. Energy profiles and barriers in the ordered KTP-LiVPO₄F structure for two pathways. Dark red color is our work, whereas lavender blue is from the work by H. Kim *et al.* [1]. (A) Energy profile and (B) Li-ion migration along Path 1; (C) energy profile and (D) Li-ion migration along Path 2.

Supplementary note 2. Structure optimization.

A) Molecular dynamics.

To determine the positions of Li atoms within the KTP-LiVPO₄F structure, we employed structure optimization using simulated annealing via *ab initio* molecular dynamics (AIMD) simulations. Initially, the structure was heated from 100 to 600 K over the time of 1 ps followed by the structure annealing at 600 K for 2 ps. These calculations were performed in the NVT ensemble with the Andersen thermostat.

Subsequently, the last structure after the annealing process was fully optimized at 0 K. The equation of state is shown in Figure S4. The optimized lattice constants are provided in Table S6. The crystal structure is shown in Figure S5. Notably, the relaxed structure has disordering in the Li sublattice, albeit the overall framework retained the KTP structure. At 0 K, the energy of our structure is -6.913 eV/atom, which closely aligns with the value of -6.917 eV/atom recalculated for the structure reported by H. Kim *et al.*, characterized by the ordered Li framework [1]. The energy difference of 4 meV/atom could be easily compensated by entropic contributions due to Li disordering, favoring our structure even at room temperature.

An attempt to symmetrize the structure by using a set of several Li atoms in the optimized positions and employing symmetry operations of the KTP structure (S.G. #33 *Pna2₁*) resulted in significant forces acting on atoms, which were impossible to optimize. Conversely, the structure obtained through (AIMD) simulations demonstrated reliable optimization to near zero forces and proved to be dynamically stable, suggesting a more reasonable structural configuration. We performed annealing of our and H. Kim structures at temperatures of 300, 600, and 800 K, each for a duration of 3 picoseconds. Subsequently, we did ionic relaxation of structures at 0 K. For our structure, the ratio of Li atoms occupying the Li(I) and Li(III) positions to those in the Li(II) position remained consistent across all three temperatures. In the Kim structure, Li atoms remained in Li(I) positions for temperatures of 300 and 600 K. These observations underscore the significance of finite temperature effects in an adequate sampling of Li atoms in the KTP-LiVPO₄F structure. Notably, even within a brief simulation time of 3 ps and a high temperature of 800 K, we observed disordering of the Li sublattice in the ordered structure of H. Kim.

Table S6. Unit cell parameters calculated with DFT and refined from XRD experiments for the KTP-LiVPO₄F. The reference data is taken from the work by H. Kim *et al.* [1].

Method	a , Å	b , Å	c , Å	α , °	β , °	γ , °	Volume, Å ³
Calculations (our)	12.934	6.344	10.774	90	90	90	884.148
Experiment (our)	12.9376(12)	6.3355(6)	10.5103(16)	90	90	90	861.49(18)
Calculations from [1]	12.946	6.429	10.723	90	90	90	892.443
Experiment from [1]	12.817(8)	6.395(4)	10.600(5)	90	90	90	868.826

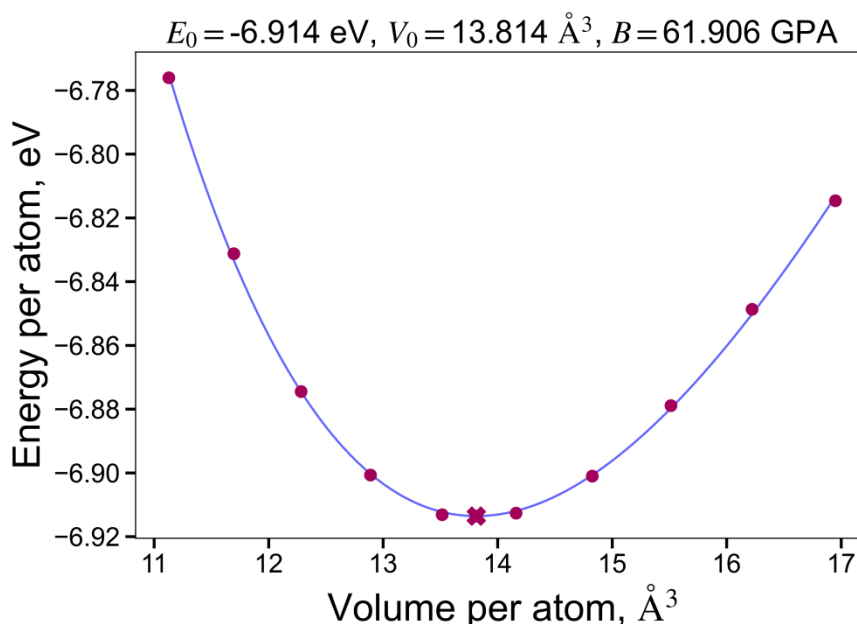


Figure S4. PBE+ U calculated equation of state for KTP-LiVPO₄F.

To demonstrate the difference between ordered ([1]) and disordered (our work) Li frameworks, we present a superimposed image of two structures, as shown in Figure S5. In the ordered structure, Li atoms occupy the centers of the voids, whereas in the disordered structure, Li atoms can also occupy the voids edges. This disordering phenomenon is not observed in KTP-AVPO₄F (A = K, Na, Rb) as the ionic radius of the corresponding ions is considerably larger than that of Li. Consequently, only Li ions can be situated at void edges, whereas Na, K, and Rb ions are unable to do so due to their larger ionic radii.

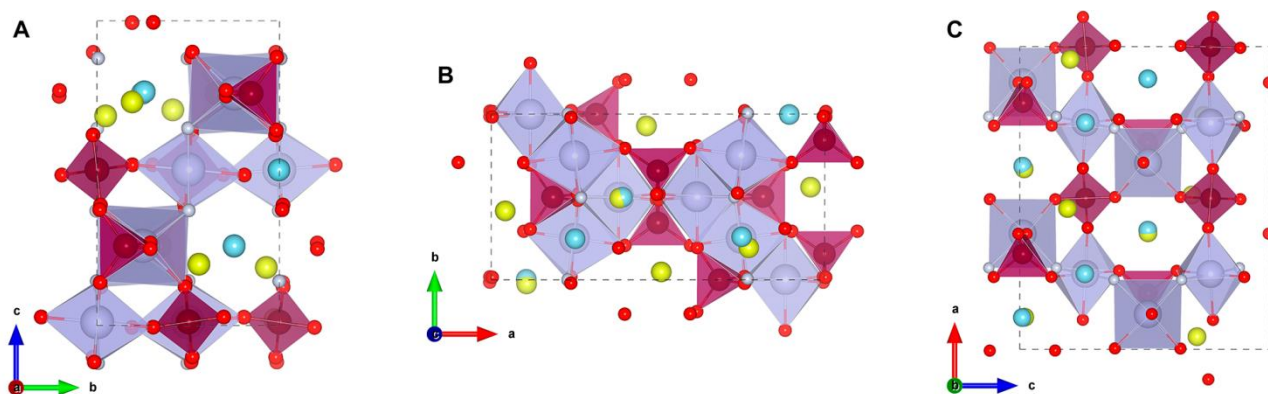


Figure S5. The crystal structure of KTP-LiVPO₄F after optimization with DFT. Yellow atoms – this work, cyan atoms are taken from [1]. The perspectives in the (A) *bc* plane, (B) *ab* plane, (C) *ac* plane.

A schematic representation of one of the voids in the KTP framework is shown in Figure S6. Throughout AIMD simulations, Li⁺ ion migrates from the void center to the edge, positioning itself between two vanadium atoms. As a result, the average Li–V bond lengths have a decrease of 0.2 Å.

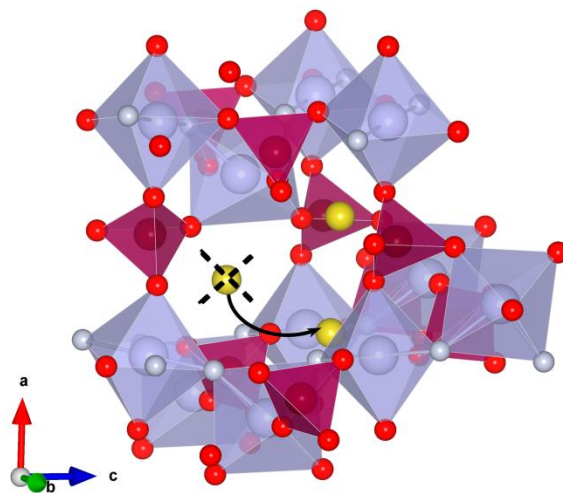


Figure S6. Schematic transition of the Li(II) to Li(I) position. The initial position Li(II) is crossed, while the final position is indicated with the arrow direction.

B) Li coordination and bond distances.

In contrast to KTP-AVPO₄F (A = Na, K, Rb) structures, where M ions may occupy various positions in the voids, the KTP-LiVPO₄F structure exhibits a distinct behavior, wherein lithium ions are categorized into three distinct types. Li(I) forms a tetrahedron with four O atoms. Li(II) resides within a plane alongside four O atoms. Li(III) is located in one plane with two O and two F atoms. Experimental and calculated bond lengths for three types of Li atoms are provided in Table S7. The visual representation is shown in Figure S7. The difference in experimental and calculated Li(III)–O(9) bond lengths is because of Li positioning in the Li(III)O₂F₂ rhomboid coordination, but the same general shape.

Table S7. Selected interatomic distances in units of Å for KTP-LiVPO₄F (S.G. #33, *Pna2*₁). Experimental bond lengths are calculated from powder X-ray diffraction data. Calculated values are derived as average from the DFT calculations.

Polyhedron	Bond type	Calculated bond length, Å	Experimental bond length, Å
Li(I)O ₄	Li(I)–O(1)	1.91	1.9(2)
	Li(I)–O(2)	1.95	2.1(2)
	Li(I)–O(3)	2.08	2.2(2)
	Li(I)–O(4)	2.32	2.3(3)
Li(II)O ₄	Li(II)–O(5)	1.99	2.0(3)
	Li(II)–O(6)	2.04	2.2(2)
	Li(II)–O(7)	2.23	2.2(3)
	Li(II)–O(8)	2.65	2.4(2)
Li(III)O ₂ F ₂	Li(III)–F(1)	1.98	2.1(2)
	Li(III)–F(2)	2.00	2.1(3)
	Li(III)–O(9)	1.98	2.5(3)
	Li(III)–O(10)	2.80	2.6(3)

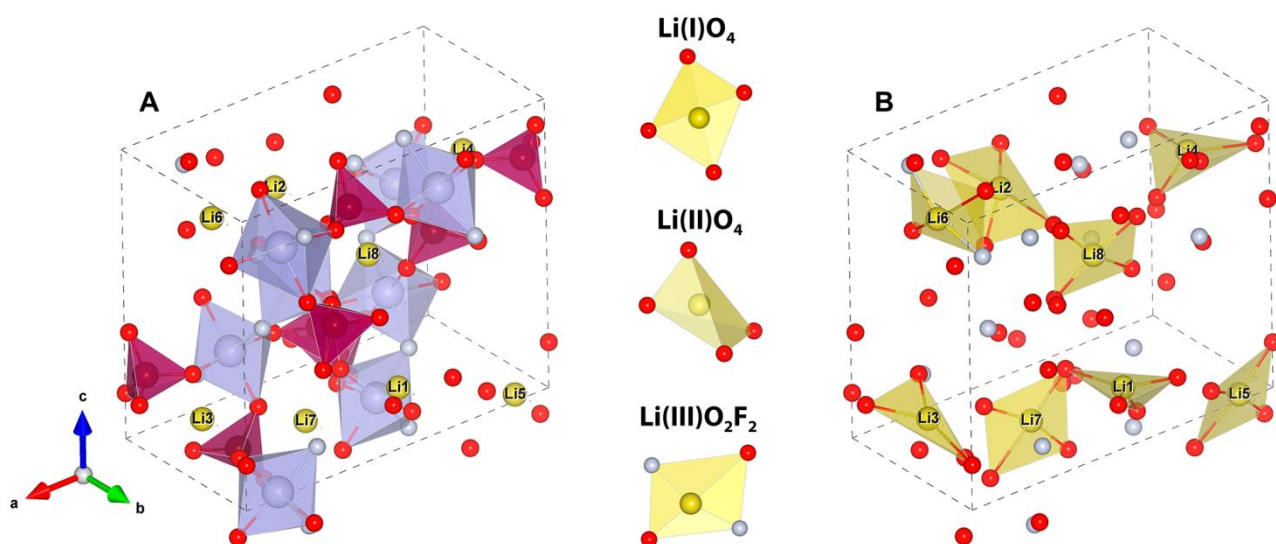


Figure S7. Crystal structure of the KTP-LiVPO₄F and polyhedra inside it. (A) Li atoms in the framework of other elements. (B) Li polyhedra surrounded by O and F atoms.

Supplementary note 3. Phase diagram.

To find the stability region of KTP-LiVPO₄, we constructed the Li–V–P–O–F phase diagram. For that, we fully optimized crystal structures using data from the Materials Project Database [2]. The following phases were used: Na (mp-127), V₂O₅ (mp-25279), V₂O₃ (mp-21579), VO₂ (mp-19094), tavorite LiVPO₄F (mp-25423), PO₂ (mp-562065), P₂O₅ (mp-2173), PO₄ (mp-72666), Li₃V₂PO₄ (mp-6396), Li₃V₂(PO₄)₃ (mp-1199961), LiV₂(PO₄)₃ (mp-26123), Li₂V₂(PO₄) (mp-26957), LiVO₂ (mp-19340), Li₄P₂O₇ (mp-28450), Li₄P₂O₇ (mp-554577), Li₂O (mp-1960), LiF (mp-1138), VF₂ (mp-555934), VF₃ (mp-555931), VF₄ (mp-555799), VF₅ (mp-27309).

For convenience of comparison with other studies, the chemical potentials were taken with respect to reference phases by introducing $\Delta\mu_i$ as

$$\Delta\mu_i = \mu_i - \mu_i^0,$$

where μ_i^0 is the chemical potential of element i in the reference phase, such as metallic Li, bcc-V, bcc-P, F₂ molecule, and O₂ molecule with overbinding correction ($\mu^0(\text{O}_2) = E_{\text{tot}}(\text{O}_2)/2 + 0.68 \text{ eV}$) [3]. The temperature and oxygen partial pressure contributions to μ_{O} are defined using the ideal gas expression [4] as follows:

$$\Delta\mu_{\text{O}}(T, P) = \Delta\mu_{\text{O}}(T, P_0) + \frac{1}{2} k_{\text{b}} T \ln\left(\frac{P}{P_0}\right) \quad (\text{S1})$$

where $P_0 = 1$ atmosphere, and $\Delta\mu_{\text{O}}(T, P_0)$ represents the variation of μ_{O} with temperature at the ambient pressure, which is available in NIST tables [5,6].

Under equilibrium conditions the chemical potentials should satisfy the following criteria:

$$\mu_{\text{Li}} + \mu_{\text{V}} + \mu_{\text{P}} + 4\mu_{\text{O}} + \mu_{\text{F}} = H_{\text{f}}(\text{LiVPO}_4\text{F}) \quad (\text{S2})$$

$$\sum_i m_i(\text{end-member}) \Delta\mu_i \leq \Delta H_{\text{f}}(\text{end-member}) \quad (\text{S3})$$

where $\Delta H_{\text{f}}(\text{LiVPO}_4\text{F})$ and $\Delta H_{\text{f}}(\text{end-member})$ are the formation enthalpies of LiVPO₄F and end-member phases, respectively. $m_i(\text{end-member})$ and $\Delta\mu_i$ represents the chemical composition of the constituent element i in each phase diagram end-member and its chemical potential. The stable range of $\Delta\mu_i$ for LiVPO₄F can be evaluated by solving Eq. (S2) and Eq. (S3).

The calculated Li–V–P–O–F phase diagram under the synthesis condition ($T = 600 \text{ K}$ and $p = 10^{-7} \text{ atm}$) is shown in Figure S8. Here, the number of dimensions is $n-2$ as the chemical

potential of O_2 is determined from the synthesis condition, and F is unambiguously determined from Equation (S2). Further, we can fix one of the chemical potentials of Li , V , and P to get the 2D cross-section of the 3D phase diagram, as shown in Figure S9.

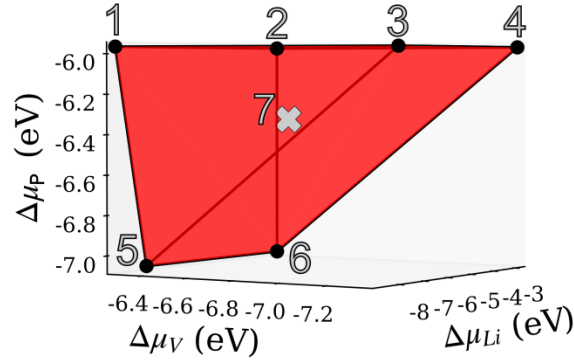


Figure S8. Phase diagram of the KTP-LiVPO₄F for the synthesis conditions with fixed oxygen chemical potential ($T = 600$ K and $p(O_2) = 10^{-7}$ atm). The red area corresponds to the stability region.

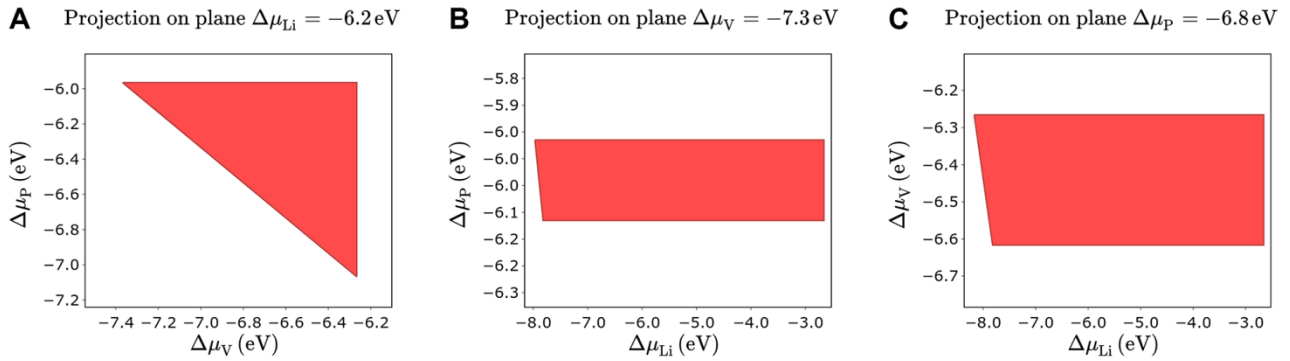


Figure S9. Cross sections of the KTP-LiVPO₄F phase diagram. The red area corresponds to the stability region. The chemical potentials for the variable elements were fixed for one of the elements at arbitrary levels of (A) $\Delta\mu_{Li} = -6.2$ eV; (B) $\Delta\mu_V = -7.3$ eV, and (C) $\Delta\mu_P = -6.7$ eV inside the stability region.

Table S8. Chemical potentials ($\Delta\mu_i$) of vertices and centroid point on the phase diagram as shown in Figure S8.

	$\Delta\mu_{\text{Li}}$, eV	$\Delta\mu_{\text{V}}$, eV	$\Delta\mu_{\text{P}}$, eV	$\Delta\mu_{\text{O}}$, eV	$\Delta\mu_{\text{F}}$, eV
1	−8.922	−6.266	−5.965	−1.644	4.140
2	−7.820	−7.368	−5.965	−1.644	4.140
3	−7.820	−6.266	−7.068	−1.644	4.140
4	−2.657	−7.368	−5.965	−1.644	−1.023
5	−2.657	−6.266	−7.068	−1.644	−1.023
6	−2.657	−6.266	−5.965	−1.644	−2.126
7 (centroid)	−5.422	−6.633	−6.332	−1.644	1.375

Table S9. Chemical potentials (μ_i and $\Delta\mu_i$) in eV of selected points on the phase diagram. Here the notations Li-poor and Li-rich are regarding the chemical potential of μ_{Li} at the centroid point. Notations for the points are taken from Table S8.

	Li-poor (point 1)		Li-rich (point 6)		centroid (point 7)	
	μ_i	$\Delta\mu_i$	μ_i	$\Delta\mu_i$	μ_i	$\Delta\mu_i$
Li, eV	−10.812	−8.922	−4.547	−2.657	−7.312	−5.422
V, eV	−11.806	−6.266	−12.909	−7.369	−12.173	−6.633
P, eV	−11.341	−5.965	−11.341	−5.965	−11.708	−6.332
O, eV	−5.332	−1.644	−5.332	−1.644	−5.332	−1.644
F, eV	−0.049	1.854	−5.212	−3.309	−0.528	1.375

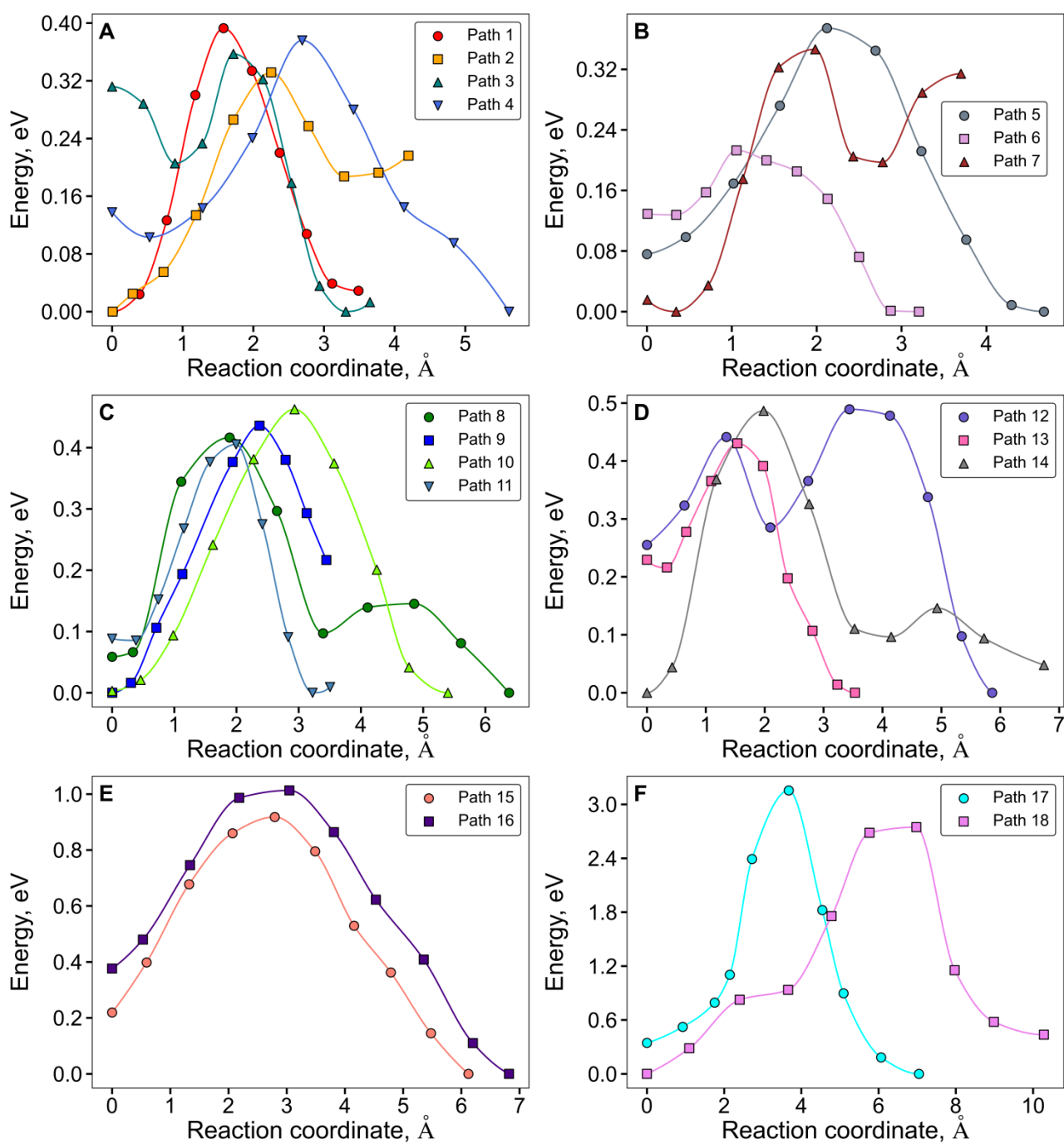


Figure S10. PBE-NEB calculated migration energy profiles in the fully inserted KTP-LiVPO₄F.

Table S10. Migration barriers in the fully inserted KTP-LiVPO₄F. Notations correspond to those in Figure S10. Migration pathways correspond to the initial and final positions of vacancies. The type of migration in the initial and final coordination of Li vacancy is classified according to Table S7. Additionally, we provide migration distance and energy barriers of those migration acts.

Notation	Migration pathway	Type of migration	Migration distance, Å	Energy barrier, eV
Path 1	Li(7)–Li(1)	Li(I)–Li(II)	3.49	0.39
Path 2	Li(8)–Li(3)	Li(I)–Li(II)	4.20	0.33
Path 3	Li(6)–Li(5)	Li(III)–Li(I)	3.65	0.36
Path 4	Li(4)–Li(4)	Li(II)–Li(II)	5.62	0.38
Path 5	Li(3)–Li(4)	Li(II)–Li(II)	4.68	0.37
Path 6	Li(6)–Li(2)	Li(III)–Li(II)	3.20	0.21
Path 7	Li(4)–Li(6)	Li(II)–Li(III)	3.70	0.35
Path 8	Li(7)–Li(3)	Li(I)–Li(II)	6.35	0.42
Path 9	Li(8)–Li(2)	Li(I)–Li(II)	3.44	0.44
Path 10	Li(8)–Li(1)	Li(I)–Li(II)	5.40	0.46
Path 11	Li(3)–Li(5)	Li(II)–Li(I)	3.50	0.41
Path 12	Li(2)–Li(7)	Li(II)–Li(I)	5.86	0.49
Path 13	Li(2)–Li(8)	Li(II)–Li(I)	3.53	0.43
Path 14	Li(8)–Li(4)	Li(I)–Li(II)	6.74	0.49
Path 15	Li(4)–Li(5)	Li(II)–Li(I)	6.12	0.92
Path 16	Li(6)–Li(6)	Li(III)–Li(III)	6.82	1.01
Path 17	Li(6)–Li(8)	Li(III)–Li(I)	7.05	3.16
Path 18	Li(3)–Li(7)	Li(II)–Li(I)	10.28	2.75

Supplementary note 4. Surface energies.

Because the $Pna2_1$ space group lacks centrosymmetry, only stoichiometric, nonsymmetric slabs can be constructed for KTP structures. In this study, we focused on surface orientations that are observed experimentally: (100), (010), (001), and (110). Due to the disordering of the Li sublattice, the total number of terminations is substantial. Therefore, we pre-selected terminations for each orientation, considering the number of broken bonds at the surfaces.

Considering that the bond strength correlates with the magnitude of the energy increase upon its breaking, our selection process prioritized minimizing broken bonds such as P–O, followed by V–(O,F), and then Li–(O,F) atoms. For each orientation, we selected 50% of terminations for the optimization. However, if all terminations had a similar degree of bond breaking, as observed with the (001) surface orientation, we considered all of them within this set of broken bonds. The total number of terminations for a given surface orientation, selection criterion and number of selected terminations are provided in Table S11.

Table S11. Surface orientation, total number of terminations, selection criterion and number of selected terminations for (100), (010), (001), and (110) surfaces. Selection criterion of termination is based on the maximum number of permitted broken bonds for the P, V, F, and O species.

Surface orientation	Number of terminations	Selection criterion, maximum number of broken bonds for P V F O	Number of selected terminations
(100)	32	2 4 2 4	16
(010)	22	4 6 4 4	10
(001)	24	2 6 2 4	20
(110)	20	6 8 6 4	8

Next, we calculated surface energies for the selected terminations according to Equation (S1). The results are provided in Table S12. Here, we limit the calculation of surface energies only to the center of the stability region.

Table S12. Slab sizes, number of broken bonds and surface energies for the selected terminations for the most important surface orientations: (100), (001), (010), (110) for the conditions at the center of the stability region (point 7 in Figure S8 and Table S9).

Termination	a , Å	b , Å	c , Å	Number of broken bonds	Surface energy, J m^{-2}
(100) surface orientation					
2	6.34	10.93	13.20	$n(\text{P})=2, n(\text{V})=2, n(\text{F})=0$	2.33
3	6.34	10.93	12.60	$n(\text{P})=2, n(\text{V})=2, n(\text{F})=0$	2.40
4	6.34	10.93	12.50	$n(\text{P})=1, n(\text{V})=3, n(\text{F})=0$	2.11
5	6.34	10.93	13.20	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	1.76
6	6.34	10.93	12.80	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	2.50
7	6.34	10.93	13.20	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	2.19
10	6.34	10.93	13.60	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	1.83
11	6.34	10.93	13.00	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	2.54
12	6.34	10.93	13.10	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	2.06
13	6.34	10.93	12.70	$n(\text{P})=1, n(\text{V})=3, n(\text{F})=0$	2.07
14	6.34	10.93	13.30	$n(\text{P})=2, n(\text{V})=2, n(\text{F})=0$	4.67
15	6.34	10.93	12.40	$n(\text{P})=2, n(\text{V})=2, n(\text{F})=0$	2.44
26	6.34	10.93	13.00	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	2.09
27	6.34	10.93	12.70	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	2.20
28	6.34	10.93	13.20	$n(\text{P})=2, n(\text{V})=4, n(\text{F})=2$	1.97
29	6.34	10.93	12.90	$n(\text{P})=1, n(\text{V})=3, n(\text{F})=0$	1.69
30	6.34	10.93	12.30	$n(\text{P})=2, n(\text{V})=2, n(\text{F})=0$	2.41
31	6.34	10.93	11.80	$n(\text{P})=2, n(\text{V})=2, n(\text{F})=0$	2.06
(010) surface orientation					
1	10.93	14.14	13.20	$n(\text{P})=6, n(\text{V})=4, n(\text{F})=2$	2.60
2	10.93	14.14	13.00	$n(\text{P})=4, n(\text{V})=6, n(\text{F})=2$	2.08

9	10.93	14.14	12.60	n(P)=4, n(V)=6, n(F)=2	2.27
10	10.93	14.14	13.30	n(P)=5, n(V)=5, n(F)=2	1.97
11	10.93	14.14	13.50	n(P)=6, n(V)=4, n(F)=2	2.35
12	10.93	14.14	13.50	n(P)=5, n(V)=5, n(F)=2	2.11
13	10.93	14.14	12.90	n(P)=4, n(V)=6, n(F)=2	2.13
20	10.93	14.14	12.60	n(P)=4, n(V)=6, n(F)=2	2.14
21	10.93	14.14	12.90	n(P)=5, n(V)=5, n(F)=2	2.48
22	10.93	14.14	13.20	n(P)=4, n(V)=6, n(F)=2	2.46
(001) surface orientation					
2	6.34	12.77	10.70	n(P)=2, n(V)=4, n(F)=2	2.86
3	6.34	12.77	10.80	n(P)=0, n(V)=6, n(F)=2	1.59
4	6.34	12.77	10.60	n(P)=0, n(V)=6, n(F)=2	1.73
5	6.34	12.77	10.50	n(P)=2, n(V)=4, n(F)=2	2.73
6	6.34	12.77	10.60	n(P)=2, n(V)=4, n(F)=2	2.57
7	6.34	12.77	10.30	n(P)=2, n(V)=4, n(F)=2	2.52
9	6.34	12.77	10.50	n(P)=2, n(V)=4, n(F)=2	2.70
10	6.34	12.77	10.10	n(P)=2, n(V)=4, n(F)=2	2.92
12	6.34	12.77	10.70	n(P)=2, n(V)=4, n(F)=2	2.54
13	6.34	12.77	10.80	n(P)=0, n(V)=6, n(F)=2	1.39
14	6.34	12.77	10.90	n(P)=0, n(V)=6, n(F)=2	1.68
15	6.34	12.77	10.80	n(P)=0, n(V)=6, n(F)=2	2.17
16	6.34	12.77	10.80	n(P)=1, n(V)=5, n(F)=2	2.61
17	6.34	12.77	10.70	n(P)=2, n(V)=4, n(F)=2	3.12
18	6.34	12.77	10.30	n(P)=2, n(V)=4, n(F)=2	2.75
19	6.34	12.77	10.50	n(P)=2, n(V)=4, n(F)=2	2.53
20	6.34	12.77	10.70	n(P)=2, n(V)=4, n(F)=2	2.71

21	6.34	12.77	10.30	n(P)=2, n(V)=4, n(F)=2	2.49
22	6.34	12.77	11.00	n(P)=2, n(V)=4, n(F)=2	2.21
23	6.34	12.77	10.30	n(P)=2, n(V)=4, n(F)=2	3.08
(110) surface orientation					
7	10.93	14.14	11.20	n(P)=6, n(V)=4, n(F)=2	2.34
8	10.93	14.14	10.90	n(P)=6, n(V)=6, n(F)=2	2.97
9	10.93	14.14	10.60	n(P)=4, n(V)=6, n(F)=2	2.08
12	10.93	14.14	10.50	n(P)=4, n(V)=6, n(F)=2	2.64
13	10.93	14.14	10.60	n(P)=4, n(V)=6, n(F)=2	2.48
15	10.93	14.14	11.20	n(P)=4, n(V)=6, n(F)=2	2.25
16	10.93	14.14	11.30	n(P)=6, n(V)=6, n(F)=2	3.03
17	10.93	14.14	10.70	n(P)=6, n(V)=4, n(F)=2	2.22

For each surface orientation, terminations with the lowest and second lowest energies were used for the bond recovery procedure, prioritizing P atoms over V atoms, over Li atoms. In instances where two terminations with the same set of broken bonds exhibited similar surface energies, both were considered for the bond recovery procedure, as in the case of 3rd and 13th terminations of the (100) surface orientation.

The KTP-LiVPO₄F has two different VO₄F₂ polyhedra in its framework, as shown in Figure S11. In the *trans*-VO₄F₂, F atoms are symmetrically positioned with respect to the V atom, whereas in the *cis*-VO₄F₂, F atoms share a common edge. Therefore, it is not always possible to recover broken bonds around V atoms unambiguously. For instance, if we have the basis of VO₁F₁ atoms, there can be two types of recovered polyhedra and with different orientations. In such cases, we opted for the type of the polyhedron that maintains the ordering of polyhedra within the KTP framework in bulk.

Furthermore, the orientation of the PO₄ polyhedron can vary at the surface if it has more than two broken O bonds. To address such scenarios, we explored multiple ways of the broken bonds' recovery for the 5th termination of the (100) surface orientations. The results show that the difference in surface energies of differently oriented PO₄ polyhedra is only 0.01 J/m². Consequently, we selected the orientation of PO₄ arbitrarily in the process of broken bond recovery.

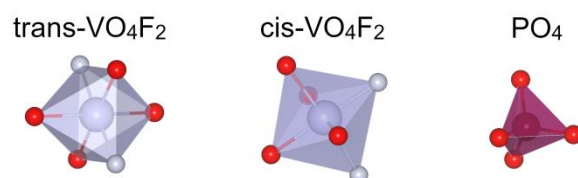


Figure S11. Polyhedra in the KTP-LiVPO₄F structure. In *trans*-VO₄F₂, F atoms are located symmetrically with respect to V(*trans*) atom, whereas in *cis*-VO₄F₂, F atoms share one edge.

The results on broken bonds recovery are provided in Table S13. In all cases, the procedure leads to the decrease in surface energy, ranging from 0.18 to 1.45 J m⁻². Negative surface energies for the conditions of Li reduction are attributed to the way of phase diagram construction. As we considered a limited number of end-members, the actual stability range may be narrower than that calculated. Adding more end-members, some regions of the phase diagram can be removed, leading to the narrowing of stability range. As a result, edges of stability regions will potentially give only positive surface energies. Therefore, we considered the center of the phase diagram, as it most closely resembles the synthesis conditions, and used these conditions to calculate surface energies for subsequent analyses.

In our approach, we focused on recovering the broken bonds around cations (P, V, F) with anions (O, F), consequently leading to an increase in the number of broken bonds around anions. This increase also contributes to the overall surface energy. It is plausible that alternative combinations of recovered bonds could potentially be more effective, further reducing surface energies. However, despite this uncertainty, the general trend consistently resulted in a decrease in surface energies after V and P broken bond recovery.

Table S13. Recovery of broken bonds for the (100), (001), (010), and (110) surface orientations. Bond recovery types, energies per atom, non-stoichiometric elements and surface energies under three conditions (Li-rich, Li-poor and centroid condition) are provided in Table S9.

Recovery type	Non-stoichiometric elements	Surface energy, J/m ² (Li-poor)	Surface energy, J/m ² (Li-rich)	Surface energy, J/m ² (centroid)
5 th termination of (100) surface orientation; n(P)=2, n(V)=4, n(F)=2 broken bonds				
None	—	1.76	1.76	1.76
V bond (×2)	O=2	1.40	1.40	1.40
P bond (x2) (oriented bottom)	O=2	1.12	1.12	1.12
P bond (x2) (oriented left)	O=2	1.11	1.11	1.11
V and P bond (x2)	O=4	1.25	1.25	1.25
P, V, F bonds	O=4 F=2	−0.45	1.94	0.83
13 th termination of (100) surface orientation; P=1, V=3 broken bonds.				
None	—	2.07	2.07	2.07
P bonds	O=1	1.50	1.50	1.50
P and V bonds	O=4	1.89	1.89	1.89
3 rd termination of (001) surface orientation; n(V)=6, n(F)=2 broken bonds.				
None	—	1.59	1.59	1.59
V bonds	O=4	1.10	1.10	1.10
V bonds	O=4 F=2	−0.96	1.09	0.14
13 th termination of (001) surface orientation; n(V)=6, n(F)=2 broken bonds				

None	—	1.39	1.39	1.39
V bonds	O=4	1.14	1.14	1.14
V bonds	O=4 F=2	−0.74	1.30	0.35
10 th termination of (010) surface orientation; n(P)=5, n(V)=5, n(F)=2 broken bonds				
None	—	1.97	1.97	1.97
P and V bonds	O=7	1.51	1.51	1.51
9 th termination of (110) surface orientation; n(P)=6, n(V)=4, n(F)=2 broken bonds.				
None	—	2.08	2.08	2.08
P and V bonds	O=8	1.61	1.61	1.61
P and V bonds	O=8 F=2	1.13	2.2	1.71
17 th termination of (110) surface orientation; n(P)=6, n(V)=4, n(F)=2 broken bonds				
None	—	2.22	2.22	2.22
P and V bonds	O=8	1.46	1.46	1.46
P bonds	O=6	1.40	1.40	1.40
P and V bonds	O=8 F=2	0.84	1.90	1.41

Next, we investigated the behavior of surface energies for slabs with P and V broken bonds and those subjected to the bond recovery procedure as a function of temperature. The results are depicted in Figure S12. Within the typical synthesis temperature range of 550-650 K, slabs with recovered broken bonds consistently exhibited lower surface energies compared to those with broken bonds. This observation suggests that the surfaces of KTP-LiVPO₄F tend to minimize the number of P and V broken bonds.

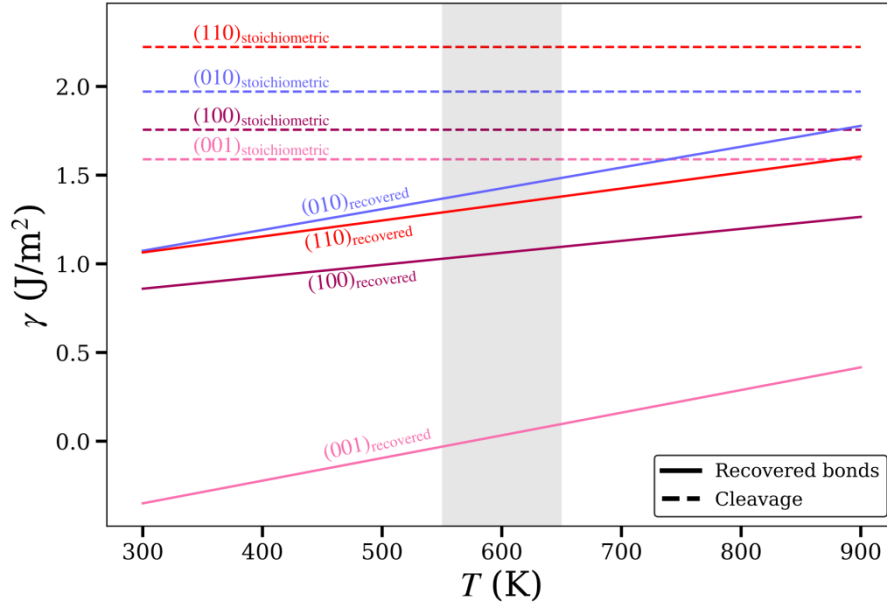


Figure S12. Surface energies as functions of temperature of KTP-LiVPO₄F for the (100), (001), (010) and (110) surface orientations. Dashed lines are stoichiometric structures with broken bonds, solid lines are non-stoichiometric structures after the bond recovery procedure. The gray hatched area corresponds to the typical synthesis temperatures of 550-650 K. Here, we considered chemical potentials from the center of stability range (the centroid point in Table S9).

As the absolute values of surface energies depend on bond strength in material, they cannot be used to evaluate structure's stability by themselves. Therefore, we utilized the ratio between cohesive energy (E_{coh}) and surface energy (E_{suf}) as was proposed in the work by A. Boev *et al.* [7]. Maximizing this descriptor allows us to attain both a large specific area of cathode particles and high thermodynamic stability. Consequently, we define cohesive energy as follows:

$$E_{\text{coh}} = \frac{(xE_A + yE_B) - E_{A_xB_y}}{x+y} \quad (\text{S4})$$

where $E_{A_xB_y}$ is the total energy of the A_xB_y bulk unit cell, E_A , E_B are the energies of the isolated atoms A and B respectively.

In this work, we calculated the $E_{\text{coh}}/E_{\text{suf}}$ ratio for surfaces with the lowest surface energies corresponding to the (100), (001), (010), and (110) Miller indices before and after the broken bond recovery procedure. The results are shown in Figure S13. In all cases, surfaces with recovered bonds exhibited a higher ratio of $E_{\text{coh}}/E_{\text{suf}}$, which is better for cathode materials. Moreover, the (100) and (001) orientations surpassed the proposed criterion of $70 \text{ \AA}^2$ for materials with large

surface area, as suggested by the authors of the former article. The (110) orientation displayed a ratio close to the borderline value of $63 \text{ \AA}^2$, whereas the (010) surface has a slightly lower value with the ratio of $58 \text{ \AA}^2$. Presumably, the (010) and (110) surface orientations have lower ratios as bond recovery procedures for them were not the most efficient.

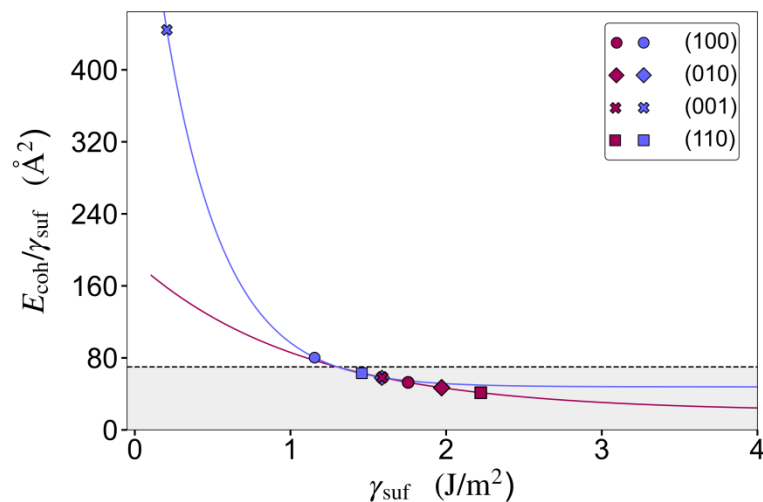


Figure S13. Ratio $E_{\text{coh}}/\gamma_{\text{suf}}$ vs. γ_{suf} for the 5th termination of the (100) surface orientation. The dashed line on $70 \text{ \AA}^2$ shows criteria for compounds with more easily formed free surfaces. Structures with broken bonds are depicted in dark red color, while structures after the broken bond recovery procedure are represented in lavender blue. Here, we considered chemical potentials from the center of stability range (the centroid point in Table S9).

Supplementary note 5. Particle morphology.

To validate the results of broken bonds recovery, we constructed Wulff shapes, using terminations with the lowest surface energies for each Miller index under annealing conditions ($T = 600$ K, $p = 10^{-7}$ atm), as detailed in Table S13. The results are provided in Table S14, and the calculated Wulff shapes are shown in Figure S14A. The difference with the micrograph shown in Figure S14C could be attributed to suboptimal procedures for broken bond recovery, as suggested by $E_{\text{coh}}/\gamma_{\text{suf}}$ for the (110) and (010) surfaces. For instance, if the procedure were more successful for the (110) orientation and its surface energies were reduced to 0.4 eV, the calculated Wulff shape and micrograph would resemble each other, as depicted in Figure S14B.

The KTP-AVPO₄F (M = Li, Na, K, Rb) structures inherit the morphology of their ammonium-containing precursor (M = NH₄), which also have a shape similar to that shown in Figure S14B. However, Wulff shapes do not always accurately reproduce particle morphologies. Therefore, to validate the results on particle shape thoroughly, it is necessary to calculate surface energies for the KTP-NH₄VPO₄F structure and consider more complex factors, such as kinetic effects, impurities, and growth conditions.

Table S14. Calculated and supposed surface energies in units of J/m² for the most important Miller indices: (100), (010), (001), and (110). Here, we considered chemical potentials from the center of stability range (centroid point in Table S9).

Surface energy	(100)	(010)	(001)	(110)
Calculated, J/m ²	0.83	1.51	0.14	1.40
Supposed, J/m ²	0.83	1.51	0.14	0.40

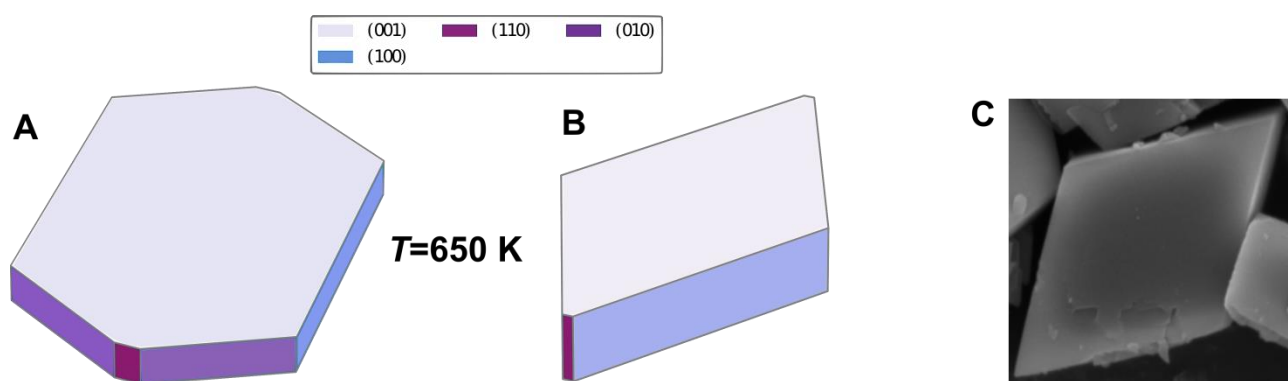


Figure S14. KTP-LiVPO₄F morphology. (A) calculated Wulff shape; (B) hypothetical Wulff shape with lower surface energy for the (110) Miller index; (C) micrograph of KTP-LiVPO₄F particle.

Supplementary note 6. Defect formation energies.

Defect formation energies were calculated for the fully charged state of battery with electric potential of 4.8 eV, $T = 300$ K, and $p = 1$ atm. The calculated chemical potentials corresponding to these conditions are provided in Table S15.

Table S15. Chemical potentials (μ_i and $\Delta\mu_i$) in eV at the voltage of 4.8 V, $T = 300$ K, and $p = 1$ atm.

	Li	V	P	O	F
μ_i , eV	-6.690	-13.276	-13.530	-4.590	-3.480
$\Delta\mu_i$, eV	-4.800	-7.736	-8.154	-0.339	-1.577

To study stability of KTP-LiVPO₄F surfaces upon cycling, we calculated defect formation energies as follows:

$$E_f = [E_{def} - E_0] + \sum_i \Delta n_i \mu_i, \quad (S5)$$

where E_{def} and E_0 are the total energies of the vacancy-containing and the initial configurations, respectively. μ_i is the chemical potential of species i under the selected conditions and n_i is the number of off-stoichiometric elements between two configurations.

In this work, we considered the following types of defects: vacancies, single and pair anti-sites. The results for the bulk KTP-LiVPO₄F structure are shown in Figure S15.

Table S16. Defect formation energies in the bulk KTP-LiVPO₄F structure. The notations and order of defects coincide with those in Figure S15. The change in total magnetic moments represents the difference before and after introduction of the defect. Here, oxidation state changes on atoms were considered if there was a magnetic moment change of more than 0.5 μ_B . Otherwise, minor changes were attributed to the oxidation of cations as “ox(Cat)” or reduction of anions as “red(An)”.

Defect number	Notation for the defect	Fundamental defect reaction	Comment on the type of defect	Defect formation energy, eV	Change in the total magnetic moment, μ_B
1	U_V'''	$V_V^\times \rightleftharpoons U_V''' + 3V_V^\bullet$	Vacancy in V(cis)	1.05	4.37
2	U_V'''	$V_V^\times \rightleftharpoons U_V''' + 3V_V^\bullet$	Vacancy in V(trans)	1.79	4.48
3	$U_F^\bullet$	$F_F^\times \rightleftharpoons U_F^\bullet + \text{ox(Cat)}$	Vacancy in F(cis)	4.65	-0.79
4	$U_F^\bullet$	$F_F^\times \rightleftharpoons U_F^\bullet + V_V'$	Vacancy in F(trans)	3.52	-0.85
5	$U_O^{\bullet\bullet}$	$O_O^\times \rightleftharpoons U_O^{\bullet\bullet} + \text{ox(Cat)}$	Vacancy in O(cis)	5.34	-0.12
6	$U_O^{\bullet\bullet}$	$O_O^\times \rightleftharpoons U_O^{\bullet\bullet} + \text{ox(Cat)}$	Vacancy in O(trans)	5.58	-0.08
7	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	Vacancy in Li(II)	-0.46	0.48
8	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	Vacancy in Li(II)	-0.63	0.45
9	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	Vacancy in Li(II)	-0.29	0.37
10	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + V_V^\bullet$	Vacancy in Li(II)	-0.52	0.58
11	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	Vacancy in Li(I)	-0.25	0.42
12	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	Vacancy in Li(III)	-0.77	0.49
13	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	Vacancy in Li(I)	-0.37	0.42
14	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + V_V^\bullet$	Vacancy in Li(I)	-0.63	0.89
15	$V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times \rightleftharpoons V_{Li}^{\bullet\bullet} + V_V''$	V in Li(II) in pos	4.32	-3.83
16	$V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times \rightleftharpoons V_{Li}^{\bullet\bullet} + V_V''$	V in Li(I) in pos	3.85	-3.80
17	$V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times \rightleftharpoons V_{Li}^{\bullet\bullet} + V_V''$	V in Li(III) in pos	3.96	-3.81
18	Li_V''	$V_V^\times \rightleftharpoons Li_V'' + 2V_V^\bullet$	Li in pos V(cis)	2.42	3.40
19	Li_V''	$V_V^\times \rightleftharpoons Li_V'' + 2V_V^\bullet$	Li in pos V(trans)	1.15	3.70
20	Li_V''	$V_V^\times \rightleftharpoons Li_V'' + 2V_V^\bullet$	Li in pos V(trans)	1.15	3.69

21	$F_O^\bullet$	$O_O^\times \rightleftharpoons F_O^\bullet + V_V'$	F in pos O in V(cis)	2.91	−0.90
22	$F_O^\bullet$	$O_O^\times \rightleftharpoons F_O^\bullet + V_V'$	F in pos O in V(trans)	2.79	−0.86
23	O_F'	$F_F^\times \rightleftharpoons O_F' + \text{ox}(\text{Cat})$	O in pos F in V(cis)	0.56	0.44
24	$O_F' + F_O^\bullet$	$O_O^\times + F_F^\times \rightleftharpoons O_F' + F_O^\bullet$	Exchange O and F in V(trans)	1.94	−0.05
25	$O_F' + F_O^\bullet$	$O_O^\times + F_F^\times \rightleftharpoons O_F' + F_O^\bullet$	Exchange O and F in V(cis)	1.84	−0.07
26	$Li_V'' + V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times + V_V^\times \rightleftharpoons Li_V'' + V_{Li}^\bullet + V_V^\bullet$	Replace Li(II) and V in V(trans)	4.08	−0.07
27	$Li_V'' + V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times + V_V^\times \rightleftharpoons Li_V'' + V_{Li}^\bullet + V_V^\bullet$	Exchange Li(II) and V in V(cis)	2.91	−0.03
28	$Li_V'' + V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times + V_V^\times \rightleftharpoons Li_V'' + V_{Li}^\bullet + V_V'' + V_V'' + \text{red}(\text{An})$	Exchange Li(I) and V in V(cis)	3.45	2.01

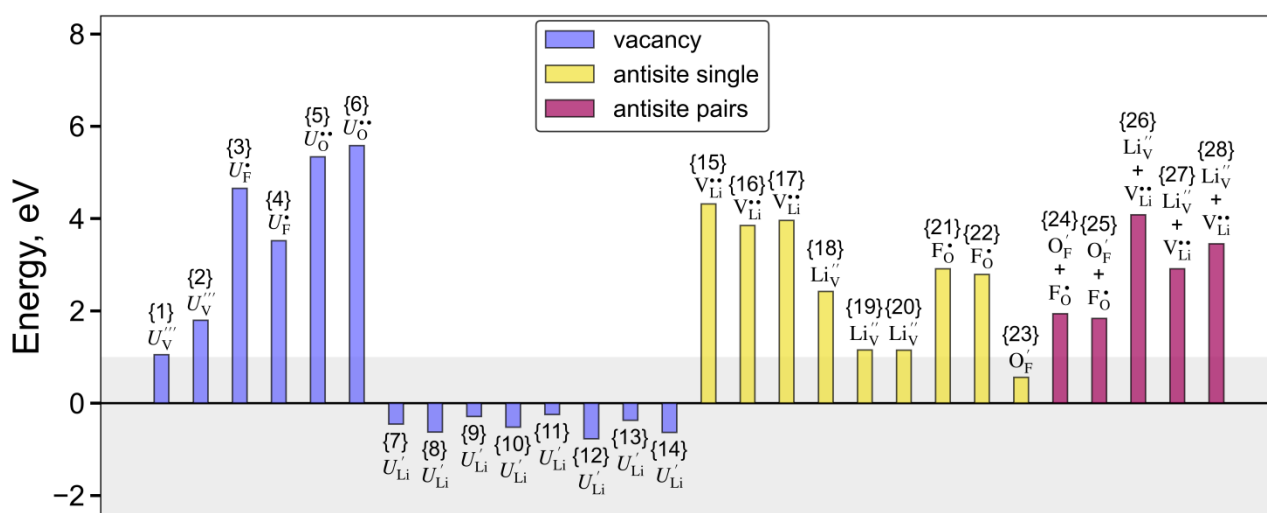


Figure S15. Defect formation energies in the bulk KTP-LiVPO₄F structure. Notation “U” is used for vacancies as we have V species in the structure. Defects in the gray hatched area are feasible ($E_{\text{def}} < 1.0$ eV). Notation numbers corresponds to those in Table S16.

Next, we calculated defect formation energies for the 5th termination of the (100) surface orientation. The results are compiled in Table S17.

Table S17. Defect formation energies for the 5th termination of the (100) surface orientation. The notations and order of defects coincide with those in Figure 5. The change in total magnetic moments represents the difference before and after the introduction of the defect. Here, oxidation state changes on atoms were considered if there was a magnetic moment change of more than 0.5 μ_B . Otherwise, minor changes were attributed to the oxidation of cations as “ox(Cat)” or reduction of anions as “red(An)”. The fundamental defect reactions were compared with those in bulk, which are presented in Table S16.

Reaction number	Notation for the defect	Fundamental defect reaction	Have similar fundamental defect reaction in the bulk	Defect formation energy, eV	Change in the total magnetic moment, μ_B
1	U_V'''	$3V_V^\times \rightleftharpoons U_V''' + V_V^{\bullet\bullet} + \text{red(An)}$	yes	3.77	3.95
2	$U_O^{\bullet\bullet}$	$O_O^\times \rightleftharpoons U_O^{\bullet\bullet} + \text{ox(Cat)}$	yes	2.83	0.66
3	$U_O^{\bullet\bullet}$	$V_V^\times + O_O^\times \rightleftharpoons U_O^{\bullet\bullet} + V_V'' + \text{ox(Cat)}$	no	2.07	-0.86
4	$U_O^{\bullet\bullet}$	$O_O^\times \rightleftharpoons U_O^{\bullet\bullet} + \text{ox(Cat)}$	yes	1.18	0.48
5	$U_O^{\bullet\bullet}$	$V_V^\times + O_O^\times \rightleftharpoons O_O^{\bullet\bullet} + V_V' + \text{ox(Cat)}$	yes	1.03	1.58
6	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	yes	-1.25	1.60
7	U_{Li}'	$Li_{Li}^\times + V_V^\times \rightleftharpoons U_{Li}' + V_V^\bullet$	yes	-2.10	1.27
8	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	yes	-1.01	0.57
9	U_{Li}'	$Li_{Li}^\times + V_V^\times \rightleftharpoons U_{Li}' + V_V^\bullet$	yes	-1.09	1.11
10	U_{Li}'	$Li_{Li}^\times \rightleftharpoons U_{Li}' + \text{red(An)}$	yes	0.30	-0.08
11	$V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times \rightleftharpoons V_{Li}^{\bullet\bullet} + \text{ox(Cat)}$	no	1.14	-2.35
12	O_F'	$F_F^\times \rightleftharpoons O_F' + V_V^\bullet$	yes	-0.07	1.49
13	$F_O^\bullet$	$O_O^\times \rightleftharpoons F_O^\bullet + \text{red(An)}$	no	1.66	-0.43
14	$F_O^\bullet$	$O_O^\times \rightleftharpoons F_O^\bullet + V_V'$	yes	0.32	0.14
15	$O_F' + F_O^\bullet$	$O_O^\times + F_F^\times \rightleftharpoons O_F' + F_O^\bullet$	yes	-0.69	1.12
16	$Li_V'' + V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times + V_V^\times \rightleftharpoons Li_V'' + V_{Li}^{\bullet\bullet}$	yes	2.59	-0.57
17	$Li_V'' + V_{Li}^{\bullet\bullet}$	$Li_{Li}^\times + V_V^\times \rightleftharpoons Li_V'' + V_{Li}^{\bullet\bullet} + V_V'' + \text{ox(Cat)}$	yes	2.29	1.04

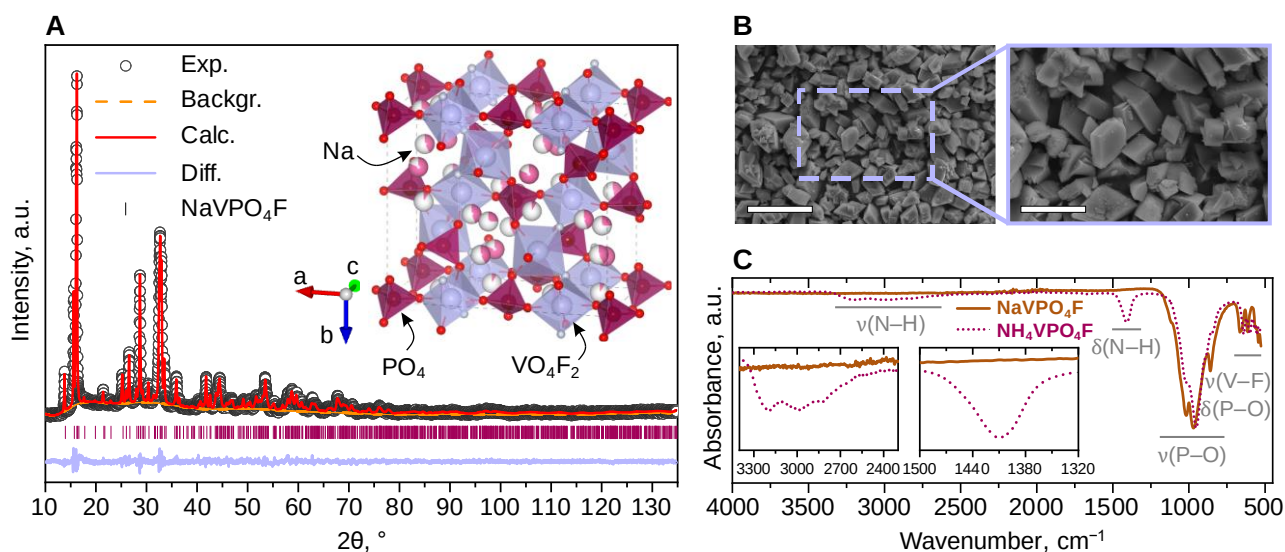


Figure S16. (A) Rietveld refinement of the KTP-NaVPO₄F X-ray powder diffraction pattern. Inset: ball-polyhedral representation of the KTP-NaVPO₄F crystal structure. (B) SEM images of KTP-NaVPO₄F powder at different magnifications of 10kX and 20kX (left and right, respectively). Scale bars are 10 and 5 μm , respectively. (C) FTIR spectra of NH₄VPO₄F and KTP-NaVPO₄F in the 4000-530 cm^{-1} range. Inserts clearly demonstrate the absence of stretching and bending modes typical for NH₄⁺.

Table S18. Atomic coordinates, occupancy factors and U_{iso} values for NaVPO₄F.

Atom	Wyckoff	x/a	y/b	z/c	$U_{\text{iso}}, \text{\AA}^2$	Occupancy
Na1	4a	0.370(20)	0.775(20)	0.036(20)	0.013(6)	0.28(6)
Na2	4a	0.372(19)	0.771(4)	0.043(19)	0.013(6)	0.45(6)
Na3	4a	0.053(1)	0.408(4)	0.705(4)	0.013(6)	0.42(2)
Na4	4a	0.498(18)	−0.122(18)	0.403(19)	0.013(6)	0.06(1)
Na5	4a	0.1074(9)	0.729(16)	0.8333(17)	0.013(6)	0.80(2)
V1	4a	0.3880(6)	0.4989(16)	0.749(3)	0.009(2)	1
V2 ⁴	4a	0.2356(7)	0.2569(17)	0	0.009(2)	1
P1	4a	0.4856(11)	0.3357(16)	0.010(4)	0.006(2)	1
P2	4a	0.1734(10)	0.517(3)	0.265(3)	0.006(2)	1
O1	4a	0.496(3)	0.471(6)	−0.111(5)	0.010(1)	1
O2	4a	0.517(3)	0.501(5)	0.110(4)	0.010(1)	1
O3	4a	0.3906(18)	0.191(5)	0.037(5)	0.010(1)	1
O4	4a	0.5898(19)	0.212(4)	0.004(6)	0.010(1)	1
O5	4a	0.108(2)	0.315(5)	0.295(4)	0.010(1)	1
O6	4a	0.069(3)	0.630(4)	0.293(4)	0.010(1)	1
O7	4a	0.253(3)	0.536(5)	0.373(5)	0.010(1)	1
O8	4a	0.234(3)	0.520(5)	0.140(5)	0.010(1)	1
F1	4a	0.278(3)	0.534(5)	0.627(4)	0.010(1)	1
F2	4a	0.259(3)	0.490(4)	0.865(4)	0.010(1)	1

⁴The z coordinate was fixed to 0 for the V2 atom to define the unit cell origin.

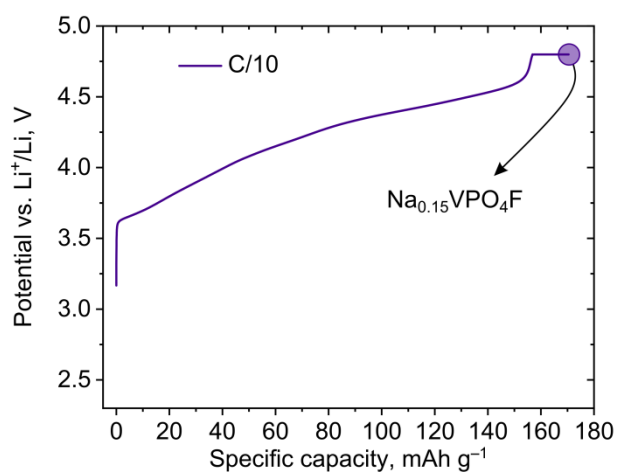


Figure S17. Galvanostatic curve illustrating the initial charge process of KTP- NaVPO_4F at C/10. 1C is equal to 156 mA g^{-1} .

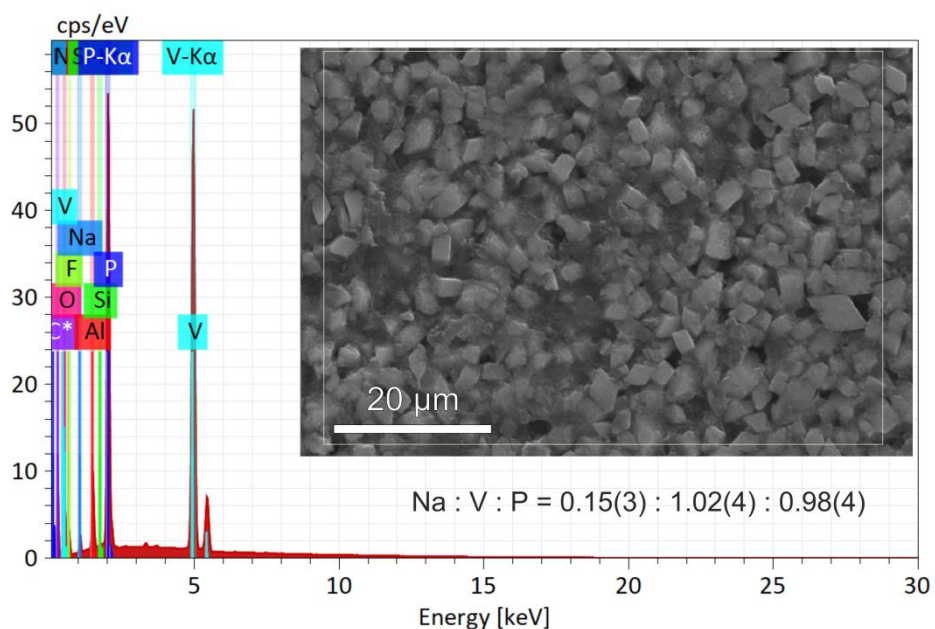


Figure S18. SEM-EDX spectrum for KTP- NaVPO_4F electrode electrochemically oxidized by charging up to 4.8 V vs. Li/Li^+ at C/10 and holding at this potential for 5 h.

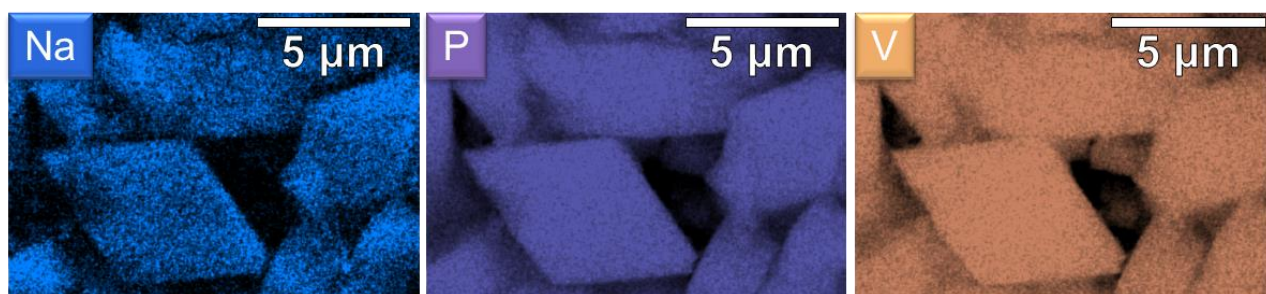


Figure S19. Compositional EDX maps of sodium, phosphorus and vanadium atoms for $\text{Na}_{0.15}\text{VPO}_4\text{F/C}$ electrode.

Supplementary note 7. Na substituting positions.

To determine the positions occupied by Na atoms in KTP-Li_{0.875}Na_{0.125}VPO₄F structure, we substituted one of Li atoms in LiVPO₄F structure with a Na atom.

To find thermodynamically favorable Na positions, we calculated the solution energy as follows:

$$E_{\text{sol}} = E_{\text{bulk}}(\text{Li}_{1-x}\text{Na}_x\text{VPO}_4\text{F}) - \sum_i \Delta n_i \mu_i, \quad (\text{S6})$$

where $E_{\text{bulk}}(\text{Li}_{1-x}\text{Na}_x\text{VPO}_4\text{F})$ is the total energy of a structure, which has a Na atom in the position of one of Li atoms. For our 64 atom supercell, $x = 1/8$. n_i and μ_i are the number of atoms in the slab and the chemical potential of species i ($i = \text{Li}, \text{V}, \text{P}, \text{O}, \text{F}, \text{Na}$), respectively. μ_{Na} is calculated using metallic bcc Na.

The calculated solution energies are provided in Table S19. The lower the solution energy, the higher the probability of Na atom to remain in this position. As a result, Na atoms in the positions of Li(II) type (planar environment) with solution energies ranging from -0.21 to -0.61 eV are more likely to occur after substitution. In contrast, the Li(I) type (tetrahedral environment, solution energies ranging from -0.05 to 0.04 eV) and Li(III) type (LiO₂F₂ polyhedron, solution energy is 0.644 eV) are more likely to be occupied by Li in the Li_{0.875}Na_{0.125}VPO₄F structure.

Summarizing, if Na atoms are present in KTP-Li_{1-x}Na_xVPO₄F structure, Li(II) types, which have high migration barriers, are suppressed to form. As a result, Li(I) and Li(III) types with low migration barriers should be dominant. This dominance should lead to an increase in the ratio of active lithium ions. Furthermore, Na⁺ ions are active, as shown in our previous work, so they should not block Li channels [8]. For instance, Na⁺ can migrate to a nearby vacancy, thereby facilitating the migration of Li⁺ ions through their initial positions.

Table S19. Substituting position for Na atom and its type in the KTP-Li_{0.875}Na_{0.125}VPO₄F structure. Solution energies (E_{sol}) are provided.

Atomic position	Position type	Solution energy, eV
Li(1)	Li(II)	−0.594
Li(2)	Li(II)	−0.614
Li(3)	Li(II)	−0.209
Li(4)	Li(II)	−0.522
Li(5)	Li(I)	0.040
Li(6)	Li(III)	0.644
Li(7)	Li(I)	−0.050
Li(8)	Li(I)	−0.022

Supplementary note 8. Molecular dynamics with machine-learning potentials.

A) MTP parameters and training details.

For the machine-learning potential (MLIP) training, we constructed $1 \times 2 \times 1$ supercells based on the conventional LiVPO_4F cell. In the Li-pristine sample, we introduced four random vacancies at Li sites, resulting in 12 out of 16 available positions being occupied by Li atoms ($\text{Li}_{12/16}\text{VPO}_4\text{F}$, 124 atoms). For the Na-substituted sample, we replaced two randomly selected Li atoms with Na atoms and similarly introduced four random vacancies in Li sites, resulting in 10 out of 16 positions occupied by Li atoms ($\text{Li}_{10/16}\text{Na}_{2/16}\text{VPO}_4\text{F}$, 124 atoms). Prior to performing AIMD simulations, we optimized the lattice constants of supercells, with the results provided in Table S20.

Table S20. Lattice constants and volumes of the simulated supercells for Li-pristine and Na-substituted structures, which we used for the AIMD simulations and the DFT calculations during the active learning stages of MTP training.

Structure	a , Å	b , Å	c , Å	V , Å ³
Li-pristine	12.638	12.551	10.816	1715.524
Na-substituted	12.689	12.601	10.859	1736.272

To mitigate the potential inaccuracies arising from improper calculations of magnetic moments during AIMD simulations and single-point calculations throughout the active learning process, we disabled spin-polarization in the DFT calculations. We evaluated both spin-polarized and non-spin-polarized setups using single instances of Li-ion migration, computed via the DFT-NEB method. One such test is illustrated in Figure S20. The results indicate that the influence of spin-polarization on the migration barriers is negligible.

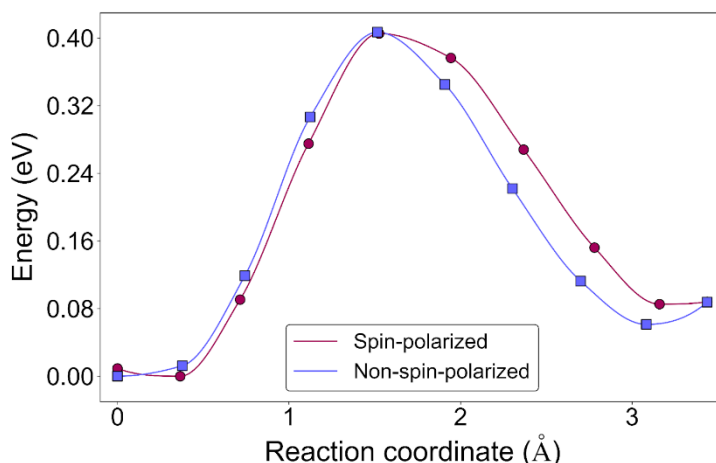


Figure S20. An instance of single migration act calculated with the DFT-NEB approach for the spin-polarized and non-spin-polarized cases.

To achieve force-field descriptions with DFT-level precision, we employed machine-learning interatomic potentials (MLIP) in the Moment Tensor Potentials (MTP) flavor [9]. The training parameters were tuned to standard values of 1, 0.1, and 0.01 for energies, forces, and stresses, respectively. We set the extrapolation threshold and threshold-brake grade to 2.0 and 35.0, respectively. To accelerate MTP training, we employed active learning [10]. During the first stage, we utilized an MTP potential with level 8 to select most of the necessary configurations. In the second stage, a level 16 MTP potential was employed for improved accuracy in fitting the results.

We computed MD trajectories at 600 K and 1200 K over 3000 timesteps, each 2 fs long, yielding a total simulation time of 6 ps for each trajectory. Overall, we collected 6000 configurations both for Li-pristine and Na-substituted samples. From these, we selected a minimal set of structures that adequately represented the configurational space. The first and second stages of active learning were then executed. During active learning, structures were collected while heating from 0 K to 600 K (or 1200 K), using a heating rate of 1.2 K fs^{-1} (or 2.4 K fs^{-1}) followed by annealing at 600 K (or 1200 K) for 1 ns. Consistent with the AIMD simulations, we used the NVT ensemble with a Nose-Hoover thermostat. Detailed information on the passive and active learning stages is provided in Table S21.

Table S21. Number of configurations after the passive learning and active learning stages for the Li-pristine ($\text{Li}_{12/16}\text{VPO}_4\text{F}$) and Na-substituted structures ($\text{Na}_{2/16}\text{Li}_{10/16}\text{VPO}_4\text{F}$).

Structure	Passive learning stageenergy	Active learning stage 1 (MTP level 8)	Active learning stage 2 (MTP level 16)
Li-pristine	483	750	2129
Na-substituted	561	983	2499

To validate the MTP training results, we evaluated the model's ability to predict energies, forces, and stresses (EFS) for both the training configurations and those obtained from AIMD simulations. The validation outcomes are shown in Figure S21 for the Li-pristine structure and Figure S22 for Na-substituted structure. The compiled metrics, such as maximum absolute errors (MaxAE), mean absolute error (MAE), and root mean square errors (RMSE) for both structures, are provided in Table S22. The low error values and well-fitted data confirm the MTP model's ability to describe EFS in both systems accurately.

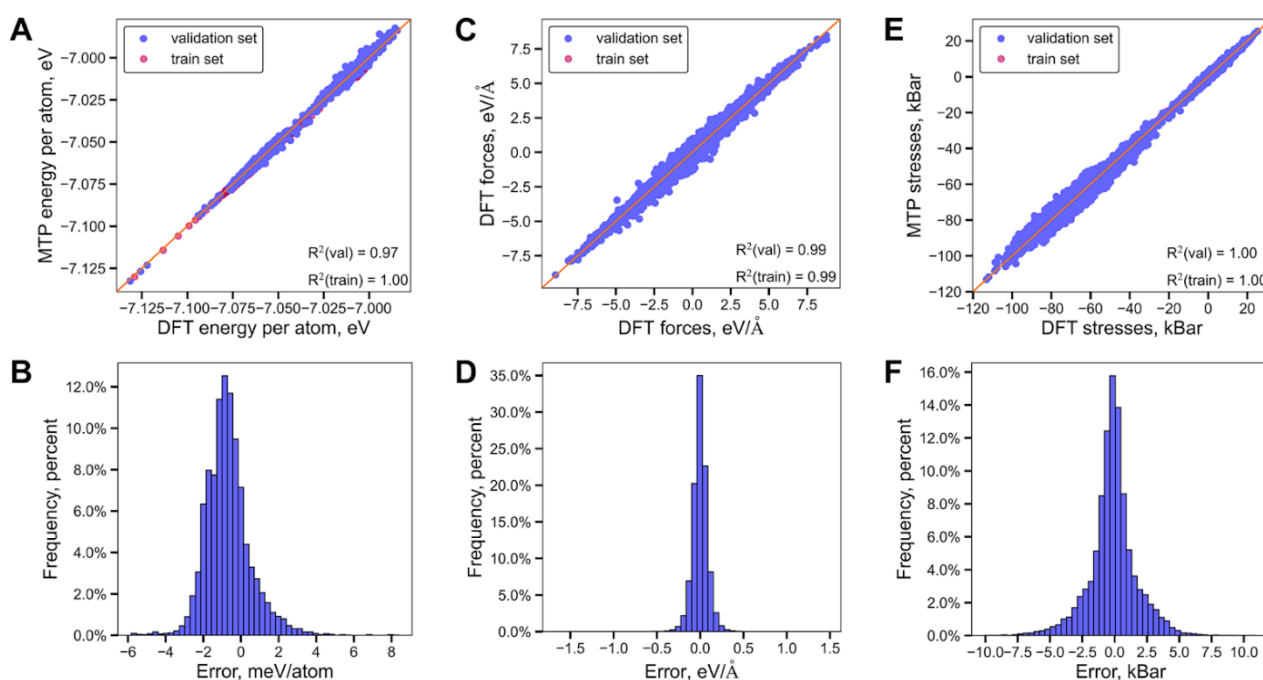


Figure S21. Calculated values and distribution of errors, obtained with the DFT method and predicted with MTP for Li-pristine structure: (A), (B) energies; (C), (D) force; (E), (F) stresses.

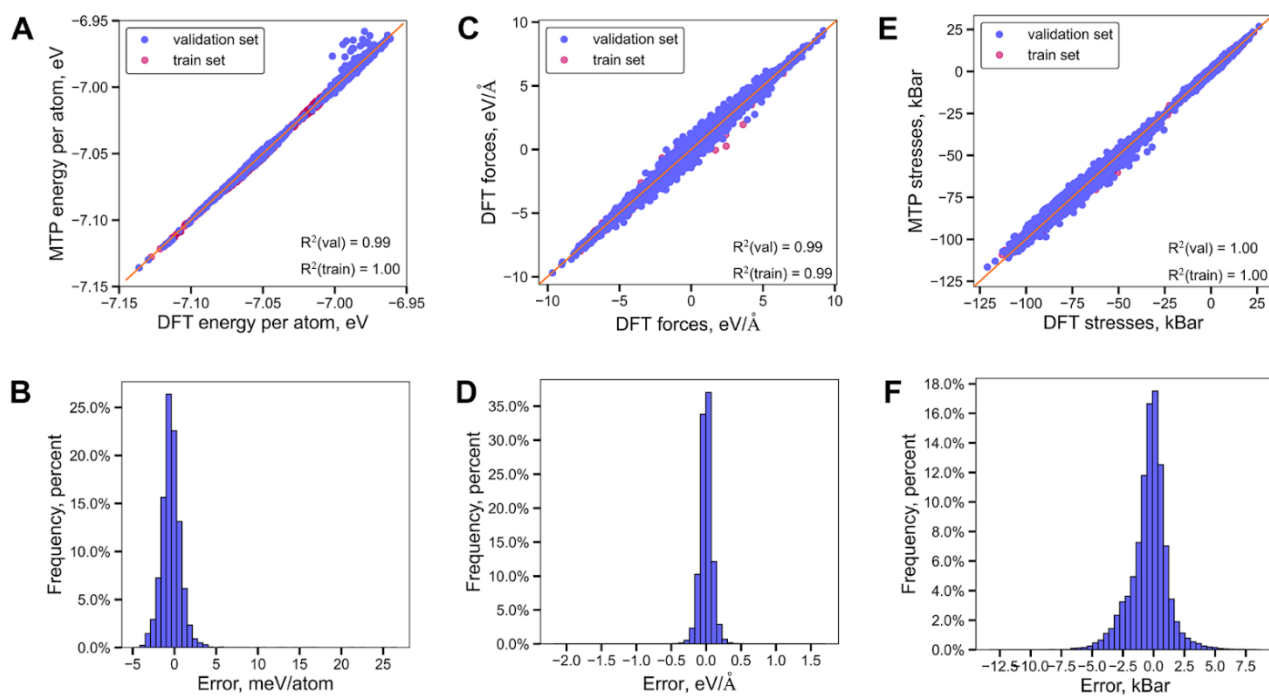


Figure S22. Calculated values and distribution of errors, obtained with the DFT method and predicted with MTP for Na-substituted structure: (A), (B) Energies; (C), (D) force; (E), (F) stresses.

Table S22. Errors of the MTP: maximum absolute errors (MaxAE), mean absolute error (MAE), and root mean square errors (RMSE). Difference between the DFT and MTP data on the training and validation sets.

Li-pristine KTP-structure			
Train set			
Number of configurations	2129		
	MaxAE	MAE	RMSE
Errors in energies, meV/atom	8.38	1.11	1.50
Errors in forces, eV/Å	1.77	0.14	0.17
Errors in stresses, GPa	1.24	0.51	0.54
Validation set			
Number of configurations	6000		
	MaxAE	MAE	RMSE
Errors in energies, meV/atom	5.82	1.10	1.32
Errors in forces, eV/Å	1.73	0.12	0.14
Errors in stresses, GPa	1.13	0.41	0.42
Na-substituted KTP-structure			
Train set			
Number of configurations	2499		
	MaxAE	MAE	RMSE
Errors in energies, meV/atom	24.9	1.07	1.93
Errors in forces, eV/Å	2.08	0.14	0.17
Errors in stresses, GPa	1.72	0.42	0.41
Validation set			
Number of configurations	6000		
	MaxAE	MAE	RMSE
Errors in energies, meV/atom	5.82	1.10	1.32

Errors in forces, eV/Å	1.77	0.12	0.14
Errors in stresses, kBar	1.13	0.41	0.42

B) Molecular dynamics simulations.

For the study of ionic diffusion, we used the $4 \times 8 \times 4$ supercells (3347 atoms), constructed from the conventional LiVPO_4F cell, using a similar approach as that for AIMD simulations. During the MD simulations, we ensured each configuration's grade does not exceed the required values of 2. Firstly, we heated from 0 K to the required temperature during 200 ps. Next, structures were annealed at the given temperature during 2×10^6 timesteps with the timestep of 0.5 fs (1 ns in total). The ranges of temperatures were 300–600 K and 400–700 K, with the step of 100 K for Li-pristine and Na-substituted structures, respectively.

The results on MD simulations are shown in Figure 7. The most important data from diffusion is provided Table S23. The following discussion is provided in the main part of the article.

Table S23. Activation energies (E_a), pre-exponential factor (D_0), room temperature diffusion coefficient ($D(T=300 \text{ K})$) and ionic conductivity ($\sigma(T=300 \text{ K})$) for Li-ion in Li-pristine and Na-substituted structures.

Structure	E_a , eV	D_0 , cm^2/s	$D(T=300 \text{ K})$, cm^2/s	$\sigma(T=300 \text{ K})$, S/cm
Li-pristine	0.356	1.8×10^{-8}	6.6×10^{-14}	2.4×10^{-7}
Na-substituted	0.204	2.4×10^{-8}	8.8×10^{-12}	1.1×10^{-4}

C) Analysis of MD simulations.

To understand the enhanced Li-ion diffusion observed in the Na-substituted structure compared to the Li-pristine structure, we examined the local environments surrounding the Li and Na ions. Initially, we calculated the distance from each ion to the center of the polyhedra formed by the six nearest O and F atoms. This metric, referred to as the distortion of atom i , is defined as follows:

$$\xi_i = \left| r_i - \left(\frac{1}{6} \sum_{n(O,F)=1}^6 r_n \right) \right| \quad (S7)$$

where r_i is the position of atom i ; r_n is the position of the n^{th} nearest atom within species O or F.

The calculated mean distortion ξ_i over simulation time for Li atoms in the Li-pristine structure and both for Li and Na atoms in the Na-substituted structure are presented in Figure S23. First, we compared ξ_i for our LiVPO₄F ordered structure with the disordered structure from the work by H. Kim *et al.* [1]. Our ordered structure shows a mean distortion of 0.82 Å, while Kim's disordered structure exhibits a significantly lower mean distortion of 0.06 Å. This minimal distortion in Kim's structure can be attributed to the small displacements of Li atoms from the centers of voids; in contrast, the KTP-MVPO₄F structures (where M = Na, K, Rb) display a distortion value of zero. In the Na-substituted structure, the mean distortion for Na atoms over the simulation time is 0.41 Å, whereas for Li atoms, it is 0.53 Å. This indicates that, on average, Na atoms are positioned closer to the centers of the voids than Li atoms during the MD simulation. As both ion species are mobile, they inevitably migrate to the edges of the voids, which explains high distortion values. Furthermore, the mean distortion for Li atoms in the Li-pristine structure is 0.58 Å, compared to 0.53 Å in the Na-substituted structure. This suggests that Li atoms occupy positions farther from the void centers in the Li-pristine structure than in the Na-substituted structure. Consequently, Li-ions in the Li-pristine structure more frequently occupy the edges of the voids than those in the Na-substituted structure.

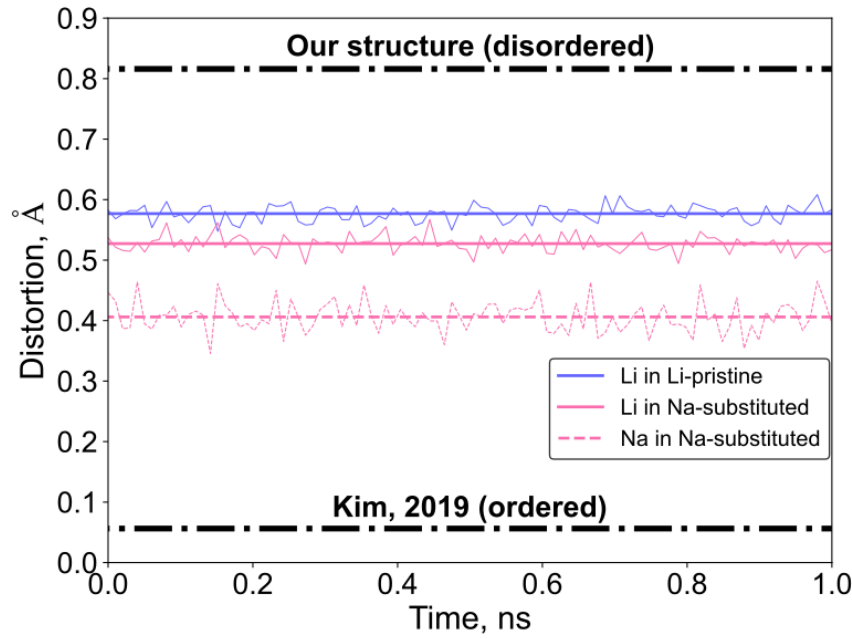


Figure S23. Mean distortion ξ_i for Li atoms in the Li-pristine structure, Li and Na atoms in the Na-substituted structure over simulation time. Dashed with dot lines are reference values of ordered LiVPO₄F structure (our work) and disordered LiVPO₄F structure (work by H. Kim *et al.* [1] are provided).

To characterize migration channels, we calculated poly-disperse Voronoi volumes, using OVITO software [11]. The mean Voronoi volumes for Li-pristine and Na-substituted structures are shown in Figure S24A. In the Na-substituted structure, the mean Voronoi volume for Li-ions is 33.2 Å³, which is larger than the 32.1 Å³ observed in the Li-pristine structure. Larger Voronoi volumes indicate a more central position inside migration channels, suggesting that Li-ion diffusion in the Na-substituted structure is facilitated compared with the Li-pristine structure due to a flattened potential energy surface. The minor difference in the volume can be attributed to the fact that during diffusion, Li ions occupy similar volumes at the transition state when migrating from one void to another. Additionally, Na-ions exhibit significantly larger mean Voronoi volumes (48.5 Å³) in the Na-substituted structure compared to Li-ions (32.1 Å³), indicating the central positions of Na atoms within the void.

To characterize distortion of Li and Na sites alternatively and remove an effect of different sizes of migration channels, we calculated the cavity radius as the distance for the particles' position to the farthest vertex of its Voronoi polyhedron and then normalized it per Voronoi volume. We name the calculated value as the mean reduced cavity radius and denote it as follows:

$$R_{red} = \sum_i r_i^c / r_i^0 = \sum_i r_i^c / (V_i^0)^{1/3} \quad (\text{S8})$$

where r_i^c is the cavity radius of atom i ; r_i^0 is the radius of the sphere, which has the same volume as the Voronoi polyhedron of atom i .

The calculated mean reduced cavity radii for both structures are presented in Figure S24B. Li-ions in the Na-substituted structure exhibit a smaller R_{red} of 0.94, compared to that of 0.95 in the Li-pristine structure. Lower values of R_{red} indicate less distortion of the Voronoi polyhedra, suggesting that atoms are positioned closer to the center of the void. Therefore, this finding aligns with the distortion values ξ_i presented in Figure S23. Additionally, Na ions in the Na-substituted structure demonstrate less distortion, with R_{red} of 0.88, which also correlates well with findings for atoms' distortion ξ_i for sodium.

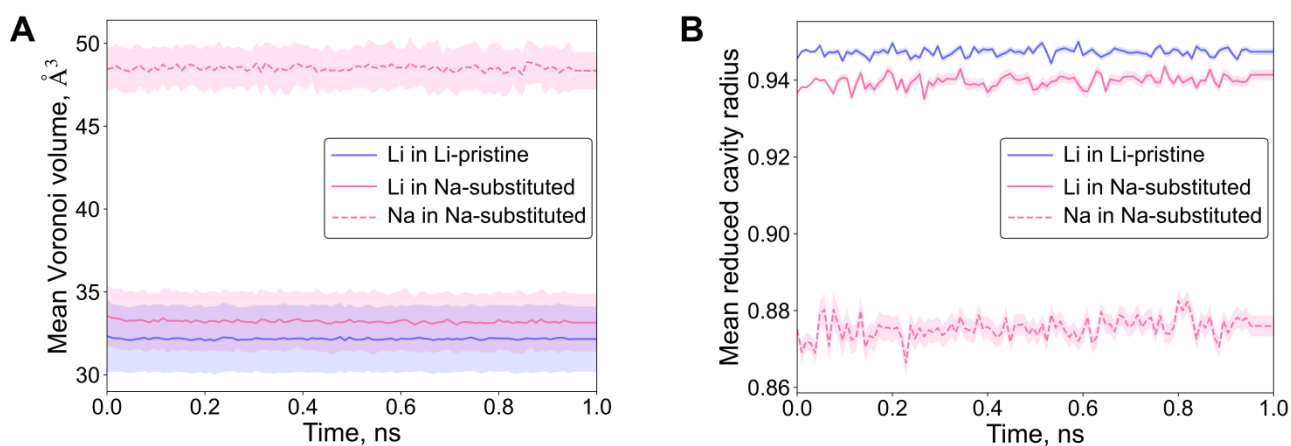


Figure S24. (A) Polydisperse Voronoi tessellation, which considers the radii of particles. (B) Distance from the particle center to the farthest vertex of its Voronoi polyhedron.

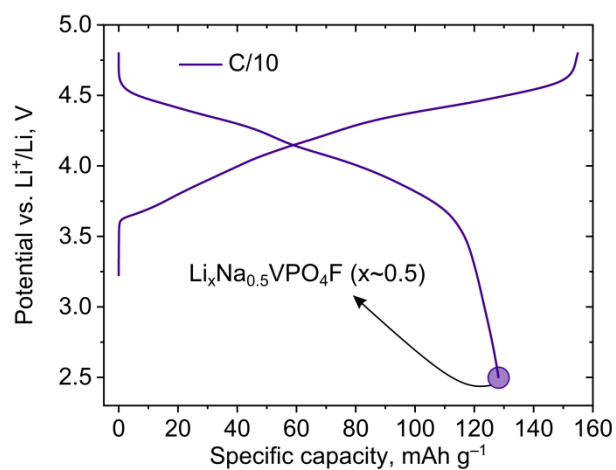


Figure S25. Charge-discharge curve of KTP-NaVPO₄F in a two-electrode cell with a lithium metal anode at C/10 (charge-discharge current 15.6 mA g⁻¹).

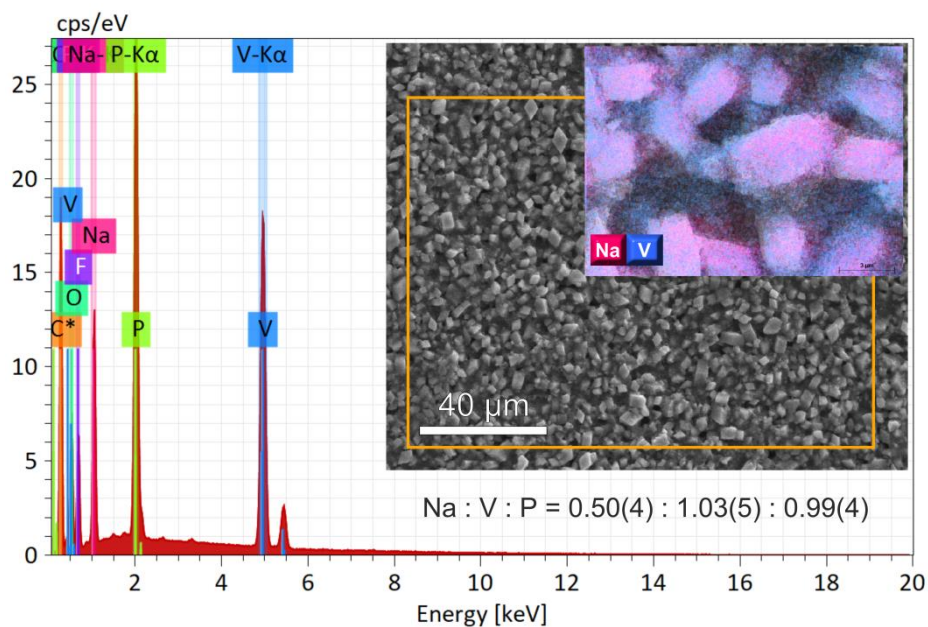


Figure S26. SEM-EDX spectrum for KTP-NaVPO₄F electrode after the first charge-discharge cycle with a lithium metal anode at C/10 (charge-discharge current 15.6 mA g⁻¹).

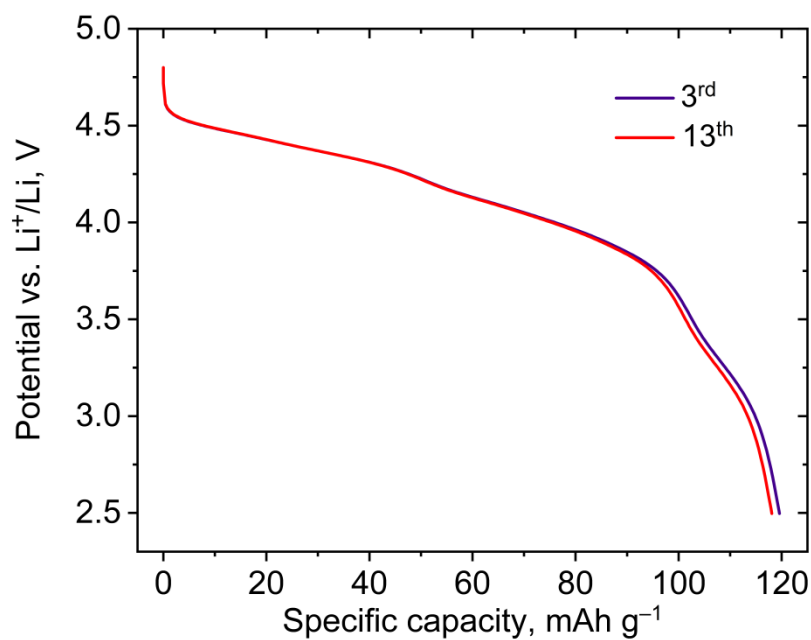


Figure S27. Results of galvanostatic cycling of $\text{KTP-Li}_x\text{Na}_{0.5}\text{VPO}_4\text{F}$ ($x \sim 0.5$) in the potential range 2.5-4.8 V vs. Li^+/Li (3^{rd} and 13^{th} cycles, C/2 charge-1C discharge).

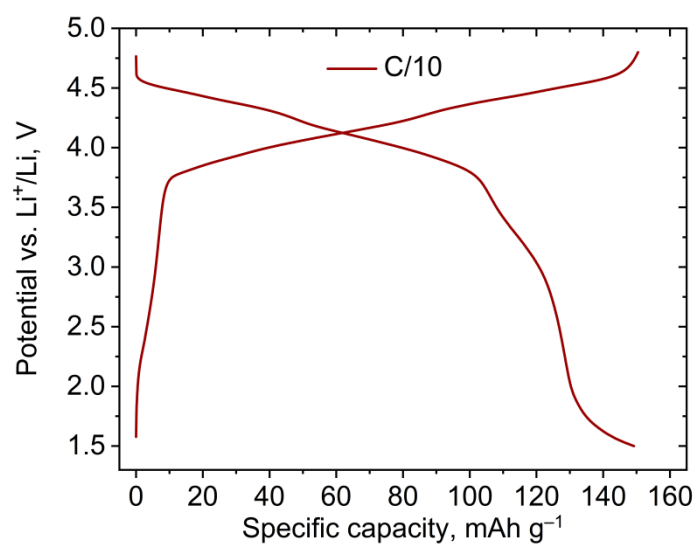


Figure S28. Results of galvanostatic cycling of $\text{KTP-Li}_x\text{Na}_{0.5}\text{VPO}_4\text{F}$ ($x \sim 0.5$) in the potential range 1.5-4.8 V vs. Li^+/Li at C/10 (charge-discharge current 15.6 mA g^{-1}).

Supplementary note 9. Chemical synthesis in the Li-V-P-O-F system.

We have found that only 4 compounds in the Li-V-P-O-F system have been described previously, namely, $t\text{-LiVPO}_4\text{F}$ [12], $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$ [13], $\text{Li}_4\text{V}(\text{PO}_4)_2\text{F}_2$ [14] and $\text{Li}_5\text{V}_2\text{PO}_4\text{F}_8$ [15]. The first one was pioneered by Barker's group in the beginning of 2000-s. It is isostructural to the nature-occurred mineral tavorite. The crystal structure of LiVPO_4F (in the space group $P\bar{1}$) motif represents a system of VO_4F_2 octahedra, which are connected through F atoms. As a result, infinite $-\text{V}-\text{F}-\text{V}-\text{F}-\text{V}-$ helical chains running along the [001] direction are formed. They are linked to each other via phosphate tetrahedra – this leads to the generation of a 3D framework, in which “tunnels” aligned along [100], [010], [101] can be observed. The latest combined X-ray and neutron diffraction studies allowed to locate Li atoms – in the frame of this model it is considered that only one crystallographic position of Li exists and Li atoms are five-coordinated (Figure S29) [16]. Notably, LiVPO_4O and LiVPO_4OH also adopt the same crystal type [17]. Key case studies of tavorite-structured electrode materials are summarized in a Table S24.

Briefly, both solid-state (and related techniques, such as sol-gel treatment of initial reaction mixture) and hydro/solvo-thermal routes are relevant for the stabilization of Li-based tavorites. The other two compositions are closely related to each other. Particularly, $\text{Li}_4\text{V}(\text{PO}_4)_2\text{F}_2$ was stabilized by the delithiation of the $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$. $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$ crystallizes in the $P2_1/c$ space group. This monoclinic lattice is composed of alternatively stacked Li and V fluoride-phosphate sheets. Vanadium octahedra are connected only through the PO_4 tetrahedra, with no V–V bonds existing in this fluoride-phosphate. Two types of alkali metal cation conduction pathways can be seen: the first one is along the a -axis and the second one – in the (100) plane. Their intersection was considered as an origin of three-dimensional conductivity. Results of electronic conductivity measurements ($1.6 \cdot 10^{-8} \text{ S cm}^{-1}$) are in line with mentioned above structural features; however, its electrochemical performance cannot be improved by conventional carbon-coating due to the low thermal stability. Deinsertion of one Li atoms per f.u. leads to formation of a rather similar host. Further delithiation is accompanied by formation of V^{5+} and associated with irreversible structural transformations. Finally, fluoride-phosphate $\text{Li}_5\text{V}_2\text{PO}_4\text{F}_8$ has been reported to have a three-dimensional framework of corner-sharing VO_2F_4 octahedra and PO_4 tetrahedra [15]. The material exhibited a reversible capacity of $\sim 110 \text{ mAh g}^{-1}$; however, like all high-voltage vanadium-based compounds, it suffers from vanadium dissolution and is accompanied by electrolyte decomposition. As a result, the material shows low Coulombic efficiency and poor cycling stability.

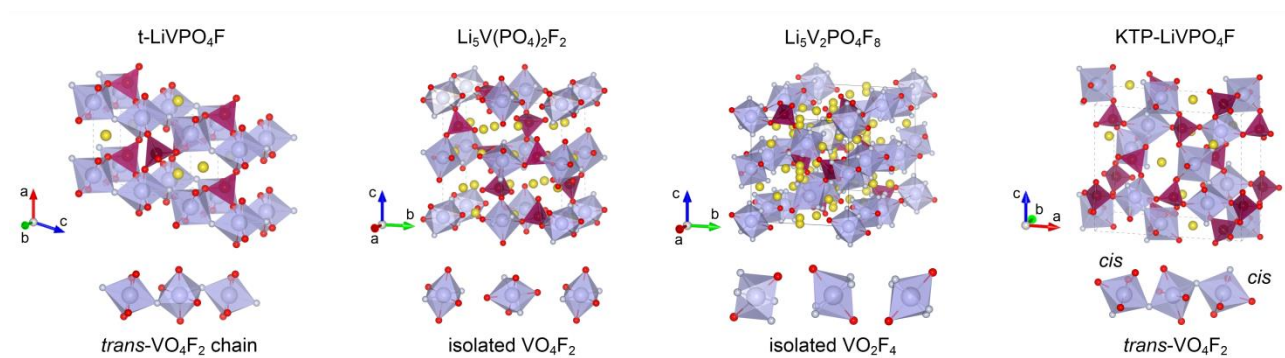


Figure S29. Summary of reported compounds in the Li-V-P-O-F system in comparison with the developed KTP-LiVPO₄F.

Also, synthesis aspects of the AVPO₄F series can be summarized (Table S25). Direct heat treatment of stoichiometric vanadium phosphate with LiF leads to the formation of tavorite-structured fluoride-phosphates [18]. The same procedure as with NaF, in the most cases, allows to isolate Na₃V₂(PO₄)₂F₃ or its partly oxidized counterparts [19–22]. Finally, annealing of VPO₄ with KF/KHF₂ or with RbF leads to the formation of the KTiOPO₄-structured fluoride-phosphates [23,24]. Involvement of hydro-/solvothetmal techniques allows to expand the synthetic playground. For instance, a Na-bearing tavorite, i.e., NaVPO₄F, was isolated for the first time under hydrothermal conditions [25]. At the same time, solid-state synthesis of this compound is a sophisticated procedure, which has been successfully performed only several times [26,27]. Noteworthy, hydrothermal treatment of a mixture, containing K, V, P, O and F sources also leads to the stabilization of KTP frameworks, KVPO₄F [28,29]. Finally, advanced synthesis design creates vaster opportunities for isolation of novel phases with more attractive functional properties, such as recently reported KTP-NaVPO₄F. A key feature of the KTP-NaVPO₄F synthesis is a low-temperature ion-exchange step that is performed with the parent framework (NH₄VPO₄F) [8,30].

Table S24. Comparison of synthetic conditions for the Li-V-P-O-F system.

Compound	Reagents	Number of stages; duration of stage; temperature	Comments	Reference
Tavorite LiVPO ₄ F	V ₂ O ₅ , NH ₄ H ₂ PO ₄ , C (Super P), LiF	2, 4 h (750°C), 48 h (250°C)	Solid state route (Carbo- thermal reduction, CTR)	[31]
		2, 4 h (750°C), 48 h (250°C)	Solid state-assisted hydrothermal synthesis	
	V ₂ O ₅ , NH ₄ H ₂ PO ₄ , H ₂ C ₂ O ₄ ·2H ₂ O, LiF	2, 5 min (2.450 Hz) × 2 times	Microwave-assisted synthesis	[32]
	V ₂ O ₅ , NH ₄ H ₂ PO ₄ , C (super P), LiF	3, 8 h (300°C), 10 h (800°C), 1 h (750°C)	Solid state synthesis	[16]
Tavorite LiVPO ₄ O	V ₂ O ₃ , NH ₄ H ₂ PO ₄ , Li ₃ PO ₄	2, 5 h (300°C), 10 h (800°C)	Solid state synthesis	[16]
Tavorite LiVPO ₄ F _{1-y} O _y	VOSO ₄ , (NH ₄) ₃ PO ₄ , (NH ₄) ₂ HPO ₄ , (NH ₄)H ₂ PO ₄ , H ₂ O	3, 8 h (300°C), 10 h (800°C), 3 days (210°C)	Solid state-assisted hydrothermal synthesis	[33]
Li ₅ V(PO ₄) ₂ F ₂	NH ₄ VO ₃ , (NH ₄) ₂ HPO ₄ , LiF, Li ₃ PO ₄	3, 2 h (350°C), 3 h (900°C), 15 min (700°C)	Solid state route, quenching is necessary	[13,34]

*Reduction of vanadium (V⁵⁺ to V³⁺) in all cases was conducted under inert (Ar/N₂) or reducing media (N₂/H₂).

Table S25. Selected synthetic conditions for the A-V-P-O-F (A = Na, K) systems.

Compound	Reagents	Number of stages; duration of stage; temperature	Comments	Reference
Tavorite NaVPO ₄ F	VPO ₄ or VPO ₄ /C, NaF	2, 2 h (650°C, 2 nd step)	Solid state synthesis, quenching is necessary	[26,27]
	VCl ₃ , Na ₃ PO ₄ ·8H ₂ O, H ₃ PO ₄ , NaF	1, 24 h (240°C)	Hydrothermal synthesis, elements ratio Na/V/PO ₄ /F: 3.3/1/1.9/1.2	[25]
Na ₃ V ₂ (PO ₄) ₂ F ₃ or its oxygenated analogues*	VPO ₄ or VPO ₄ /C, NaF	2, ≥8 h (700°C, 2 nd step)	Solid state synthesis	[35]
KTP- NaVPO ₄ F	VOSO ₄ ·3H ₂ O, NH ₄ H ₂ PO ₄ , (NH ₄) ₂ HPO ₄ , N ₂ H ₆ SO ₄ , NH ₄ HF ₂ (synthesis of NH ₄ VPO ₄ F); Monosodium glutamate hydrate	2, 1 h (215°C), 10 h (190°C)	Mild ion-exchange with the precursor obtained by hydrothermal route (structural motif of a parent compound is preserved)	[8,30]
KVPO ₄ F**	NaF, VCl ₃ , H ₃ PO ₄ , KOH	1, 5 days (180°C)	Hydrothermal synthesis	[29]

*Typical example is provided as a classical approach, which is similar to the CTR route reported for tavorite structured LiVPO₄F. Other relevant references are summarized in the previous table and in [20].

**Other case studies are summarized in [36].

Supplementary note 10. Possibility of KTP-Li_{1-x}Na_xVPO₄F ($x \sim 0.5$) practical use.

Currently, lithium cobalt oxide (LiCoO₂, LCO) remains the most widely used cathode material for lithium-ion batteries. Its specific capacity depends on the degree of lithium extraction, which is determined by the charge cutoff voltage. Most commercial models of LiCoO₂ have a cutoff voltage of 4.3 V vs. Li⁺/Li, which corresponds to a specific capacity of about 155 mAh g⁻¹ [38]. This is primarily due to safety considerations, since high extraction of Li⁺ cations can cause irreversible structural changes in the material. Lithium cobalt oxide is a virtually unrivaled component of high-power devices due to its excellent C-rate capability, compared to NMC and LFP commercial cathodes. Since our hybrid material KTP-Li_{1-x}Na_xVPO₄F ($x \sim 0.5$) also possesses an excellent C-rate capability, we decided to match it with a direct commercial analogue (Table S26). Showing comparable specific energy characteristics, the hybrid material stands out by assuming higher thermal stability and consequently safety, which motivates to continue more detailed studies of this system.

Table S26. Comparison of important characteristics of KTP-Li_{1-x}Na_xVPO₄F ($x \sim 0.5$) and LiCoO₂ [38] for use as cathode in high power devices.

	LiCoO ₂ (4.3 V cutoff)	KTP-Li _{1-x} Na _x VPO ₄ F ($x \sim 0.5$)
Operating voltage, V	3.92	4.2
Specific capacity (0.1C), mAh g ⁻¹	155	128
Energy density (0.1C), Wh kg ⁻¹	608	538
Energy density (5C), Wh kg ⁻¹	445	435
Energy density (10C), Wh kg ⁻¹	385	404
Thermal stability	Poor	Good ⁵

⁵Assumed based on the larger stability of polyanion frameworks in comparison to layered oxides.

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