Lithium iron phosphate $\text{LiFePO}_4$ (LFP) has recently emerged as an attractive cathode material for next-generation lithium ion batteries (LIBs) because of its remarkable thermal and chemical stability, nontoxicity, low cost, and reasonably high theoretical capacity ($\approx 170 \text{ mAh/g}$).\textsuperscript{12} However, the practical use of LFP is hampered by its intrinsically poor electrical and ionic conductivities.\textsuperscript{14} Considerable efforts have been made to overcome these drawbacks, including heterogeneous doping and defect engineering. For instance, aliovalent doping with Nb, Mg, Zr and Ti has been demonstrated to enhance heterogeneity doping and defect engineering. For instance, aliovalent doping with Nb, Mg, Zr and Ti has been demonstrated to enhance.

We evaluate the possible formation of recently proposed PO$_4$-deficient FePO$_4$ by calculating its structure and stability at various charge states using the DFT+U theory. Unpaired electrons resulting from PO$_4$ deficiency tend to localize on undercoordinated Fe neighbors. The absence of a PO$_4$ unit causes local lattice distortions which are found to be sensitive to the charge state. Our calculations show that neutral and negatively charged PO$_4$ vacancies may coexist under intrinsic conditions. The PO$_4$-deficient FePO$_4$ matrix turns out to be substantially softened, which may contribute to enhanced Li diffusion and provide clues toward the design of high performance LiFePO$_4$ cathode.

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Results and Discussion

As illustrated in Fig. 1a (top right inset), FePO$_4$ has an orthorhombic olivine structure (space group Pnma) where each PO$_4$ unit is connected to 5 FeO$_6$ units; Fe atoms are located on corner-sharing octahedral sites while P atoms on tetrahedral sites. The predicted lattice constants of $a = 9.97, b = 5.91,$ and $c = 4.88 \AA$ are in good agreement with the experimental values of $a = 9.7599(8), b = 5.7519(5),$ and $c = 4.7560(4) \AA.$\textsuperscript{7} The slight overestimation of lattice constant is mainly attributed to the well-known tendency of GGA to underestimate the bond strength.

Fig. 1a shows the electron density of states (DOS) projected onto Fe, P, and O atoms of pristine FePO$_4$; the top of the valence band (VB) is dominated by O 2$p$ states, whereas the bottom of the conduction band (CB) is mainly composed of Fe 3$d$ states. The predicted gap of 1.75 eV is very close to the experimental value of 1.7 eV.\textsuperscript{18} In FePO$_4$, Fe$^{3+}$ is found to have a high-spin $d^6$ electron configuration,\textsuperscript{19} yielding the fully occupied spin-up and empty spin-down states. The magnetic moment is predicted to be $4.3 \mu_B$ (per Fe), in excellent agreement with existing experimental data ($\approx 4.15 \mu_B$);\textsuperscript{14} the relatively smaller value compared to the distinct Fe$^{3+}$ case ($= 5 \mu_B$)\textsuperscript{20} is apparently attributed to the hybridization with O 2$p$ orbitals. It is also worth pointing out that the distinct overlap between P 3$d$/3$p$ and O 2$p$ orbitals is far below the Fermi level, implying the relatively stronger interaction of O atoms with P atoms than Fe atoms.

Next, we examined how the deficiency of PO$_4$ polyansors alters the electronic structure and geometry of FePO$_4$. While neighboring atoms are noticeably displaced, four of the five Fe atoms adjacent to the neutral PO$_4$ vacancy ($V^0_{PO_4}$) become fivefold coordinated and the rest is fourfold coordinated. The removal of a neutral PO$_4$ unit leaves three unpaired electrons which tend to localize on adjacent Fe atoms. As presented in Fig. 1b, the projected DOS of the PO$_4$-deficient structure exhibits two distinct defect states within the bandgap. One defect level (indicated as I) lies just above the VB, and the other (II) is in the middle of the gap. The defect state I shows overlap between spin-Up Fe 3$d$ and O 2$p$ orbitals while spreading over neighboring Fe and O atoms (as demonstrated by the band-decomposed charge density plot in Fig. 1b (top right inset); this suggests the defect level is associated with lattice distortions around $V^0_{PO_4}$. On the other hand, as shown in Fig. 1b (bottom right inset), the excess electrons associated with defect state II seem to be highly localized on three neighboring Fe atoms; this is not surprising considering that Fe 3$d$ states dominate the bottom of the CB in FePO$_4$, thus readily accepting excess electrons. Due to such charge localization, the neighboring three Fe atoms (a, b and c) are reduced to Fe$^{2+}$ [Fig. 2a]. The local lattice surrounding $V^0_{PO_4}$ exhibits an outward expansion, and the adjacent P atom is displaced slightly in [010] direction toward $V^0_{PO_4}$; consequently, the P-Fe (I)

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First Principles Prediction on the Formation and Properties of Polyion deficient Iron Phosphate

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Computational Methods

All atomic structures and energies reported herein were calculated using spin-polarized DFT within the generalized gradient approximation (GGA-PBE)\textsuperscript{11} as implemented in the Vienna Ab initio Simulation Package (VASP).\textsuperscript{12} To treat the strong on-site 3$d$ electron-electron interactions on Fe an additional Hubbard-U was added (U$_{eff} = 4.3 \text{ eV}$),\textsuperscript{13} which is a widely accepted value for the particular material system (FePO$_4$ or LiFePO$_4$).\textsuperscript{7}\textsuperscript{14}\textsuperscript{15} Renderring accurate prediction of material properties such as bandgap. The projected augmented wave method\textsuperscript{16} with a plane-wave basis set ($E_{cut} = 450 \text{ eV}$) was employed, and all atoms were fully relaxed until residual forces on constituent atoms became smaller than 1 $\times 10^{-2} \text{ eV/Å}$. The pristine FePO$_4$ was modeled using a 24-atom unit cell while the PO$_4$-deficient structure was created by removing a PO$_4$ unit from an expanded (1 $\times 2$ $\times 3$), 144-atom supercell. For Brillouin zone sampling, (3 $\times 4$ $\times 5$) and (3 $\times 3$ $\times 1$) k-point meshes in the scheme of Monkhorst-Pack\textsuperscript{17} were used for the pristine and PO$_4$-deficient cases, respectively.

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distance increases from 3.22 Å (in the pristine case) to 4.08 Å. It is worth noting that the $V_{P\alpha\beta}$-induced lattice distortion appears to be asymmetrical with respect to the (010) plane spanned by Fe (a, c and e) as the Fe (c)-(b) and (c)-(d) distances are different (4.46 and 4.54 Å, respectively). The slight deviation from symmetry is likely attributed to the unequal charge redistribution among the five Fe ions adjacent to $V_{P\alpha\beta}$, resulting in their differences in charge state and bond environment.

We also looked at the structures and relative stabilities of PO4-deficient FePO4 in positive ($V_{P\alpha\beta}^{+}$), negative ($V_{P\alpha\beta}^{-}$), and doubly negative ($V_{P\alpha\beta}^{2-}$) charge states. For $V_{P\alpha\beta}$ [Fig. 2b], with an additional hole, one of the three Fe3+ ions in $V_{P\alpha\beta}^{0}$ is oxidized to Fe4+ (a). The lattice distortion becomes symmetrical as two Fe ions (b and d) located on the opposite sides of the (010) plane have the same charge state (3+); in addition, we also found the displacement of the adjacent P atom to be much smaller if the lattice distortion was symmetrical. For $V_{P\alpha\beta}$ [Fig. 2c], the additional electron tends to localize on Fe (I), and the lattice distortion is asymmetrical. For $V_{P\alpha\beta}^{2-}$ [Fig. 2d], with additional two electrons, all five Fe3+ ions surrounding the PO4 vacancy are reduced to Fe2+, thus the symmetric configuration is restored, and the P-Fe (I) distance of 3.31 Å is very close to the pristine case (3.22 Å).

Finaly, we looked at how the PO4 deficiency affects the mechanical properties. Here we only considered the bulk modulus (B) which can be estimated by fitting the Murnaghan equation of state23 to the corresponding energy versus volume curve. Uniform tensile and compressive stress calculations are also performed to acquire the Poisson’s ratio (ν) and the shear modulus (G) of pristine FePO4. The lattice distortion is asymmetrical. For $V_{P\alpha\beta}$, the calculated FePO4 bandgap around 1.75 eV, the first donor ($E_{d1}$) correction is estimated to be smaller than 0.1 eV, which is reasonable given the considerably large dielectric constant of 17.5.22 Our calculation predicts the relative formation energies of FePO4 in different charge states with respect to $V_{P\alpha\beta}^{0}$ as a function of the Fermi level relative to the valence band maximum ($E_{F}$) for the computed FePO4 bandgap around 1.75 eV.

Figure 1. The electron density of states (DOS) projected on Fe, P and O atoms in (a) pristine and (b) PO4-deficient FePO4; the shaded gray area represents Fe 3d states, and the blue and red solid lines indicate P 3p and O 2p states, respectively [note the intensity of O 2p state in (b) is rescaled by 1/3]. The inset in (a) shows a unit cell of pristine FePO4. The band-decomposed charge densities corresponding to defect states I and II are plotted with an isosurface value of 0.005 electron/Å³ as shown in the top and bottom right insets in (b).
compressive strains were imposed on the pristine and PO4-deficient \( (V_{PO4}^0) \) FePO4 structures to achieve \( \pm 0.66\% \) volume changes.

\[
E(V) = E_0 + \left( \frac{B' V}{B} \right) \left[ \frac{(V_0/V)^{B'}}{B' - 1} + 1 \right] - \frac{V_0 B}{B' - 1} \quad [1]
\]

where \( E \) and \( E_0 \) refer to the total energies of pristine and PO4-deficient FePO4 at volume \( V \) and \( V_0 \) (equilibrium), respectively, and \( B' \) is the pressure derivative of the bulk modulus; here, we increased the cutoff energy to 550–600 eV and force tolerance to 0.01 eV/Å to refine energy variations with applied strain. While the predicted \( B \) value of 68.1 GPa for pristine FePO4 is in close agreement with previous result \( \approx 73.6 \) GPa,\(^{24} \) our calculations show a 20% reduction in \( B \) \( \approx 53.2 \) GPa with only 4.2 at.% \( V_{PO4}^0 \) in the FePO4 matrix. We anticipate such significant softening effect to have substantial impacts on Li diffusion in PO4-deficient FePO4, which is under investigation. As suggested by previous theoretical study, Li diffusion can be substantially enhanced in the strained (tensile) LiFePO4 lattice due to the excess space allowing Li migration; similar effects may be expected from the softened lattice.\(^{25} \)

### Conclusions

DFT+U calculations were performed to investigate the structure and properties of PO4-deficient FePO4 at various charge states \( (V_{PO4}^q) \). \( q \) \( \leq +1 \). The unpaired electrons associated \( V_{PO4}^q \) tend to localize on adjacent undercoordinated Fe atoms, which undergo outward displacements. The \( V_{PO4}^q \)-induced lattice distortions are found to be sensitive to \( q \). At the midgap, \( V_{PO4}^0 \) has the lowest formation energy \( (0.15 \) eV lower than that of \( V_{PO4}^0) \), but given the small energy difference, \( V_{PO4}^0 \) and \( V_{PO4}^0 \) are likely to coexist. We also find that PO4-deficiency can effectively soften the matrix as the bulk modulus \( \approx 53.2 \) GPa is reduced by 20% from the pristine case. The more flexible PO4-deficient FePO4 may thereby lower the diffusion barrier, contributing to enhanced Li mobility. Our fundamental findings shed light on a new approach to defect engineering toward the design of high performance LiFePO4 cathode.

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