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Ab Initio Identification of Li-Rich Phase in LiFePO₄

Hua Zeng, Yue Gu, Gaofeng Teng, Yimeng Liu, Jiaxin Zheng, and Feng Pan

Recent discovery of anionic redox activity in Li-rich layered compounds opens a new direction for the design of high-capacity cathode materials for lithium-ion batteries. Here we use extensive ab initio calculations, the thermodynamic existence of Li-rich phase in LiFePO₄ to form LiₓFePO₄ with x not exceeding 12.5% has been proved. Anionic redox and structural stability during delithiation are further investigated. Interestingly, it is found that LiₓFePO₄ cannot be delithiated completely and thus cannot achieve extra capacity by anionic redox activity, because the local oxygen-ion redox will cause the fracture of the rigid framework formed by phosphate tetrahedral polyanion. Although the extra capacity cannot be realized, the excess Li at Fe sites can enhance the Li diffusion along the adjacent [010] channel, and contribute to the shift from 1D to 2D/3D diffusion. This study provides a fresh perspective on olivine-type LiFePO₄, and offers some important clues on designing Li-rich cathode materials with high energy density.

Introduction

With the rapid development of transportation applications, including hybrid electric vehicles, plug-in hybrid electric vehicles (PEVs) and pure electric vehicles (EVs), batteries with high energy density are urgently demanded. Developing anode and cathode materials with high energy density for rechargeable lithium-ion batteries (LIBs) becomes the most important way to meet such requirement. LIB anodes, such as a new graphene allotrope known as graphenylene, heteroatom-doped graphene, and a compound of highly dispersed nanostructured carbon nanotubes (CNTs), graphene nanoplatelet (GNPs) flakes and carbon nanofibers (CNFs), have been found to be capable of storing lithium with higher energy density. For LIB cathode materials, traditional cathode materials have relied on cationic redox reactions, and transition metals (TM) have been considered as the sole source of cathode materials for lithium intercalation cathode to provide the charge-compensating electrons after Li-ion extraction. As a consequence, the theoretical specific capacity is limited by the number of electrons that the TM ions can exchange per unit mass. Recently, with the discovery of anionic redox activity in Li-rich layered compounds, a new design paradigm for LIB cathodes based on a cumulative cationic and anionic redox activity has attracted increasing interests. The anionic redox activity will create extra capacity beyond the theoretical TM redox capacity at a high voltage, thus to extend the design of new high-capacity cathodes. Previous reported anionic redox activities are mainly observed within the Li-excess layered TM oxides, such as layered NMC (Ni–Mn–Co), Li₂MnO₃, Li₂NiO₂MnO₃O₂, Li₁Nd₀·₃Mn₀·₃O₂ (Me = Fe³⁺, Mn³⁺ and V³⁺), Li₂Ru₂SnO₃, Li₄FeSbO₄, Li₂ZrO₂, α-Li₂IrO₃, β-Li₂IrO₃, and Li₁₊ₓIrO₄.

One critical issue of the practical application for the reported Li-rich layered materials is the capacity fading during electrochemical cycles, due to the irreversible loss of lattice oxygen during the anionic redox process. It will be interesting to know whether there is possibility to form Li-rich phase in polyanionic intercalation TM compounds (e.g., LiFePO₄ and LiFeSiO₄), as the strong P-O and Si-O covalence can stabilize the lattice oxygen during the anionic redox process. Li-rich solid solution of Liₓ₂Fe₃SiO₄ (0 ≤ x ≤ 0.3) is reported recently, but the presence of additional Li-ions are in interstitial sites, which are different from the Li-rich layered materials with additional Li-ions occupying the TM sites. Moreover, no extra capacity in Liₓ₂Fe₃SiO₄ is reported. Actually, LiₓFeSiO₄ itself can be regarded as a kind of materials with anionic redox activity, as during the delithiation of the second Li-ions, oxygen redox happens. In the crystal structure of LiFePO₄ (LFP), it is reported commercialized cathode material for rechargeable LiBs all of the oxygen-ions form strong covalent bonds with phosphorus to form the phosphate tetrahedral polyanion and generate a stable three-dimensional framework. If the Li-rich phase exists, better structural stability compared with the reported Li-rich layered materials would be anticipated when the anionic redox happens, thus leading to stable extra reversible lithium storage capacity beyond the theoretical value of LFP. Though the extra Li-excess Liₓ₀·₃Fe₀·₃PO₄ is recently synthesized, they mainly focus on the influence of the excess Li-ions (at Fe sites) on the Li-Fe anti-site defects and don’t pay attention to the possibility of anionic redox activity.

In this work, using extensive ab initio calculations, we have proved the thermodynamic existence of LiₓFePO₄ (0 ≤ x ≤ 12.5%). Interestingly, the extra capacity beyond the theoretical value of LFP cannot be achieved by the Li-rich phase, due to the structural
instability when the content of the extracted Li-ions exceeds (1-2x). Further analysis reveals that the structural instability can be attributed to that the local oxygen-ion redox will cause the fracture of the rigid framework formed by phosphate tetrahedral polyanion. Nevertheless, the Li-ion diffusivity in Li$_{1-x}$Fe$_x$PO$_4$ can be enhanced by the excess Li-ions at Fe sites, reflected by the reduced energy barrier for the Li-ion diffusion along the adjacent [010] channel and the shift from 1D to 2D/3D diffusion. Our findings provide a fresh perspective on olivine-type LiFePO$_4$ and offer some important clues on designing Li-rich cathode materials with high energy density.

**Calculation method**

All calculations were performed using the plane-wave projectoraugmented wave method, as implemented in the Vienna Ab Initio Simulation Package (VASP). The Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation (GGA) was chosen as the exchange-correlation potential. Taking account of the strong on-site Coulomb interaction (U) presented in the localized 3d electrons of Fe, the PBE+U approach was employed with the U value set to 5.3 eV in Li$_{1-x}$Fe$_x$PO$_4$. Geometry optimizations and total energy calculations were spin-polarized, using a plane-wave cutoff of 520 eV. A ferromagnetic augmented wave method, as implemented in the Vienna Ab Initio Simulation Package (VASP). The Perdew–Burke–Ernzerhof (PBE) form of generalized gradient approximation (GGA) was chosen as the exchange-correlation potential. Taking account of the strong on-site Coulomb interaction (U) presented in the localized 3d electrons of Fe, the PBE+U approach was employed with the U value set to 5.3 eV in Li$_{1-x}$Fe$_x$PO$_4$. Geometry optimizations and total energy calculations were spin-polarized, using a plane-wave cutoff of 520 eV. A ferromagnetic high-spin Fe state was assumed, and the energetic effects of the magnetic ordering were small (< 0.04 eV). All the atomic positions and cell parameters were fully relaxed using a conjugate gradient algorithm, until the force on each atom was smaller than 0.001 eV/Å, and energies were converged to within 10$^{-8}$ eV per atom. A 4×3×4 k-point grid within the Monkhorst−Pack scheme was used to sample the Brillouin zone of the Li$_{1-x}$Fe$_x$PO$_4$ supercell. The supercell containing 1×2×2 unit cells (space group Pnma) was used, which corresponded to 112 atoms/cell.

A climbing-image nudged elastic band (cNEB) method was used to calculate the energy barriers for Li-ion diffusion in the bulk Li$_{1-x}$Fe$_x$PO$_4$. The nudged elastic band (NEB) is a method for finding saddle point and minimum energy path between known initial state and final state. This method works by optimizing a number of intermediate images along the path. Each image finds the lowest energy possible while maintaining equal spacing to neighboring images. The cNEB method is a small modification to the NEB method in which the highest energy image is driven up to the saddle point. This image does not feel the spring forces along the tangent. Instead, the true force at this image along the tangent is inverted. In this way, the image tries to maximize its energy along the band, and minimize in all other directions. When this image converges, it will be at the exact saddle point. Initial state is a configuration with a Li-vacancy at one octahedral sites and a Li-ion at adjacent octahedral site. Final state is opposite to initial state. Five intermediate states are inserted. All ions were relaxed for calculations of the minimum energy pathways. The density functional perturbation theory (DFPT) was used for phonon calculations. All the atomic positions were fully relaxed until the force on each atom was smaller than 0.001 eV/Å, and energies were converged to within 10$^{-8}$ eV per atom. Phonopy was used to handle force constants gained by DFPT.

**Results and discussion**

The existence of Li-Rich phase in LiFePO$_4$.

Figure 1a shows the crystal structure of olivine-type LiFePO$_4$. It was reported to crystalize in the orthorhombic space group Pnma with $a = 10.3377$, $b = 6.0112$, and $c = 4.6950$ Å. Correspondingly, for 1×2×2 supercell, $a$, $b$, and $c$ should be 10.3377, 12.0224, and 9.390 Å, respectively. As shown in Table 1, the calculated lattice parameters of LiFePO$_4$ are $a = 10.447$, $b = 12.170$, and $c = 9.507$ Å, in satisfactory agreement with the experimental values. We constructed the initial structures of Li$_{1-x}$Fe$_x$PO$_4$ (x = 6.25% and 12.5%) by replacing Fe-ions with Li-ions. In LiFePO$_4$, all Fe-ions are coordinated with six oxygen-ions to form the FeO$_6$ octahedra, which are connected by sharing O corners to form a 2D network in bc plane. All Fe sites are equivalent, and thus there is only one doping structure when x = 6.25% (Figure 1b). For $x = 12.5\%$, there are a lot

<table>
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<th>$x$</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>$\alpha$ [°]</th>
<th>$\beta$ [°]</th>
<th>$\gamma$ [°]</th>
<th>V [Å$^3$]</th>
<th>$\Delta H_f$ [eV/f.u.]</th>
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<td>90.00</td>
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<td>12.083</td>
<td>9.506</td>
<td>90.30</td>
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<td>-13.130</td>
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</table>
of doping structures. By comparing the total energies of them, we chose the structure with the minimum total energy for the further studies. All structures of Li$_{1+x}$Fe$_{1-y}$PO$_4$ ($x = 12.5\%$) are displayed in Figure S1. The structure of Li$_{1+x}$Fe$_{1-y}$PO$_4$ ($x = 18.75\%$) is displayed in Figure S2.

Table 1 shows the variation of lattice parameters and volume of Li$_{1+x}$Fe$_{1-y}$PO$_4$ after structural optimization. With the increase of $x$, $a$ and $b$ lattices shrink a little, $c$ keeps nearly invariant, and the volume gets smaller as well. Moreover, the excess Li-ions at Fe sites change the structural symmetry, resulting in a slight structural tilt with the $\beta$ angle exceeding $90^\circ$.

To study the thermodynamic stability of Li$_{1+x}$Fe$_{1-y}$PO$_4$, we first calculate its formation energy (enthalpy), $\Delta H_f$(Li$_{1+x}$Fe$_{1-y}$PO$_4$), which is defined as the total energy change of the following reaction:

$$\Delta H_f = E_{\text{tot}}(\text{Li}_{1+x}\text{Fe}_{1-y}\text{PO}_4) - (1+x)E_{\text{crystal}}(\text{Li}) - (1-x)E_{\text{crystal}}(\text{Fe}) - E_{\text{crystal}}(\text{P}) - 2E_{\text{gas}}(\text{O}_2)$$

where $E_{\text{tot}}(\text{Li}_{1+x}\text{Fe}_{1-y}\text{PO}_4)$ is the total energy of Li$_{1+x}$Fe$_{1-y}$PO$_4$, $E_{\text{crystal}}$ ($\text{Li}$, $\text{Fe}$, and $\text{P}$) are Li, Fe and P at their most stable phases, respectively, $E_{\text{gas}}(\text{O}_2)$ is the energy of O$_2$ molecular gas. The calculated formation energies of different $x$ values are shown in Table 1. We can see that $\Delta H_f$(Li$_{1+x}$Fe$_{1-y}$PO$_4$) decreases with the increase of $x$ and it is less than zero, indicating that Li$_{1+x}$Fe$_{1-y}$PO$_4$ is thermodynamically stable. Imaginary frequency also doesn’t appear in Li$_{1+x}$Fe$_{1-y}$PO$_4$ with $x = 6.25\%$ and $12.5\%$ (Figure 2b and c), which further proves that Li$_{1+x}$Fe$_{1-y}$PO$_4$ ($x = 6.25\%$ and $12.5\%)$ are thermodynamically stable. By contrast, the phonon band structure of Li$_{1+x}$Fe$_{1-y}$PO$_4$ ($x = 18.75\%$) shows imaginary frequency (Figure 2d), which seems to contradict the result of formation energy. In fact, the formation energy is a thermal index, but the phonon band structure is a lattice dynamic index. Here, the structure conforming to the two indexes is truly thermodynamically stable. From this perspective, with the increasing content of Li-ions occupying at Fe sites, there is a limit for the $x$ value to ensure the structural stability of Li$_{1+x}$Fe$_{1-y}$PO$_4$.

**Can the Li-rich phase introduce extra capacity?**

Whether Li-rich phase Li$_{1+x}$Fe$_{1-y}$PO$_4$ is able to achieve extra capacity beyond the theoretical value of LiFePO$_4$ is an important issue we care about. The extra capacity depends on the maximum amount of Li-ions that can be extracted (also the transferable electrons). Hence, the structural stability after delithiation of Li$_{1+x}$Fe$_{1-y}$PO$_4$ is further studied. Figure 3 shows the phonon band structures of Li$_{1+x}$Fe$_{1-y}$PO$_4$ ($x = 6.25\%$, $y = 1-2x$, 1, and $1+x$). It can be seen that the structure is stable when $y = 1-2x$ (all Fe-ions are in +3 oxidation state), but unstable when $y > 1-2x$.

In addition, we also performed molecular dynamics simulations to verify the instability of Fe$_{1-x}$PO$_4$ ($x = 6.25\%$ and $12.5\%)$. Figure S3 provides the initial and final atomic configurations obtained at the time of 0 and 3 ps under room
temperature condition (300 K). It is obvious that some Fe-ions deviate from the original positions and the distances between the Fe-ions and their neighboring oxygen-ions become too large (3.5 Å) to form Fe-O bonds (the Fe-O bond lengths in LiFePO$_4$ don’t exceed 2.3 Å). The above results suggest that Li$_x$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$ and $12.5\%$) cannot be delithiated completely, and thus cannot enhance the specific capacity of LiFePO$_4$. This is different from our intuitive wish that the Li$_x$Fe$_{1-x}$PO$_4$ would introduce extra capacity for lithium storage, due to the good stability of the rigid polyanion framework with strong P-O covalence. We investigated the detailed reasons why Li-rich phase in LiFePO$_4$ cannot introduce extra capacity by the change of valence state of elements.

In Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$ and $12.5\%$), some Fe sites are occupied by Li-ions, so the valence state of Fe must change due to the charge compensation, which is confirmed by analyzing the projected electronic density of states (PDOS) of Li$_{1+x}$Fe$_{1-x}$PO$_4$. Figure 4a shows the PDOS of LiFePO$_4$. By integrating Fe 3d state (spin up and spin down) below the Fermi level, we can obtain that the magnetic moments of all Fe-ions are 3.74 $\mu_B$, consistent with the fact that Fe-ions are in the +2 oxidation state and exhibit high spin $t_{2g}(↓)t_{2g}^{3}(↑)e_g^{2}(↑)$ configuration in LiFePO$_4$. Figure 5a shows the PDOS of FePO$_4$. The magnetic moments of different Fe-ions are 4.31 $\mu_B$ consistent with the fact that Fe-ions are in the +3 oxidation state and exhibit high spin $t_{2g}^{2}(↑)e_g(↑)$ configuration in FePO$_4$. Comparing Figure 4a-c, we can see that with the increase of $x$, the Fe 3d state (spin down) gradually crosses the Fermi level, indicating that some Fe$^{2+}$ ions are oxidized to Fe$^{3+}$ state. We also calculated the magnetic moments of different Fe-ions around the excess Li-ion at Fe site for the cases of $x = 6.25\%$ and $12.5\%$ (Figure 1c). When $x$ is 6.25\%, the magnetic moments of Fe$_{1-}$, Fe$_2$, Fe$_3$ and Fe$_4$ are 3.74, 3.74, 4.07 and 4.07 $\mu_B$, respectively. Interestingly, Fe$_3$ and Fe$_4$ have been oxidized but not fully to Fe$^{3+}$. When $x$ is 12.5\%, the magnetic moments of Fe$_{1-}$, Fe$_2$, Fe$_3$ and Fe$_4$ are 3.74, 3.74, 4.31 and 4.31 $\mu_B$, respectively. Obviously, Fe$_3$ and Fe$_4$ are fully oxidized to Fe$^{3+}$. Both at $x = 6.25\%$ and $12.5\%$, the oxidized Fe-ions are Fe$_3$ and Fe$_4$, not Fe$_1$ and Fe$_2$, which can also be reflected by the shorter Fe-O bond for Fe$_3$ and Fe$_4$ in Table S1.

Furthermore, we calculate the PDOS of Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$ and $12.5\%$). As shown in Figure S4, when the content of the extracted Li-ions approaches (1-2x), the Fe 3d state (spin down) fully crosses the Fermi level, meaning that all Fe$^{3+}$ are oxidized to Fe$^{3+}$. When the content of the extracted Li-ions approaches (1+x), namely Fe$_{1-x}$PO$_4$, the O 2p state (spin up) gradually crosses the Fermi level, which means that some O-ions begin to be oxidized. Note that Figure S4 is used to illustrate how the valence state of different elements change during the delithiation of Li$_{1+x}$Fe$_{1-x}$PO$_4$, which relate to the PDOS near the Fermi level. As shown in Figure S5, during the delithiation of Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$), the PDOS of P and Li atoms are far from the Fermi level and keep nearly unchanged. Hence, we only care about the contributions of the PDOS of Fe and O when analyzing the redox process. Figure 5 shows the PDOS of O 2p orbitals of four different oxygen-ion environments in Fe$_{1-x}$PO$_4$ ($x = 6.25\%$). It can be seen clearly that O$_1$ and O$_2$ are oxidized, which are the O-ions bonding with the Li-ion at Fe site in Li$_{1+x}$Fe$_{1-x}$PO$_4$. So if Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($y > 1-2x$) existed stably, Fe-ions would keep +3 oxidation state, and...
the O-ions around the Li-vacancy at Fe site would be oxidized. The local O-ion redox would result in the fracture of the rigid framework formed by phosphate tetrahedral polyanion. This inference coincides with the above calculated phonon band structures.

In order to understand the structural instability caused by the local O-ion oxidation easily, we compared the structural distortion during delithiation. In LiFePO$_4$, FeO$_6$ octahedra are connected by sharing O corners to form a 2D network in bc plane, and the PO$_4$ tetrahedrons act as the joints to connect adjacent FeO$_6$ 2D layers. The FeO$_6$ octahedra tend to be distorted during the cationic and anionic redox, which will also lead to the shrinkage of FeO$_6$ 2D layers, but the PO$_4$ tetrahedrons between the FeO$_6$ 2D layers would prevent this distortion and shrinkage due to the strong P-O covalence.

During the process from LiFePO$_4$ to FePO$_4$ (Figure 6a), the length of Fe-O bonds shortens and lattice $a$ shrinks by 4.36% (Table 2). This process is essentially a phase transition.$^{48}$ For the Li-rich phase Li$_{1+x}$Fe$_{1-x}$PO$_4$, from Li$_{1.98}$Fe$_{1.02}$PO$_4$ to Li$_{1.93}$Fe$_{1.07}$PO$_4$ ($x = 6.25\%$) with only Fe$^{3+}$/Fe$^{4+}$ redox (Figure 6b), lattice $a$ shrinks by 3.98% and the change of length of Fe-O bonds in the FeO$_6$ octahedra is similar to the phase transition from LiFePO$_4$ to FePO$_4$. However, during the oxygen-ion redox from Li$_{1.98}$Fe$_{1.02}$PO$_4$ to Fe$_{1.07}$PO$_4$ ($x = 6.25\%$), lattice $a$ only shrinks by 0.11% and the PO$_4$ tetrahedrons cannot allow the shrinkage of FeO$_6$ 2D layers any more. In addition, different from the process with only cationic redox, the length of the bond between Fe-ion and the oxidized O-ion shortens sharply during the anionic redox, indicating another kind of phase transition aggravating the structure of Fe$_{1-x}$PO$_4$, leading to the fracture of the pretty rigid frame structure of phosphate tetrahedral polyanion. Thus, Li$_{1.98}$Fe$_{1.02}$PO$_4$ cannot be delithiated completely, and cannot introduce extra capacity beyond the theoretical value of LiFePO$_4$.

The enhanced Li-ion diffusivity in Li$_{1+x}$Fe$_{1-x}$PO$_4$.

It is widely known that Li-ions diffuse along the [010] channel in the bulk LiFePO$_4$. Li-ions hop between adjacent octahedral sites via a tetrahedron hollow formed by the edge-sharing LiO$_6$ octahedrons. Similar migration trajectories exist in the bulk Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$ and 12.5\%). As shown in Figure 7a, 1 stands for a Li-ion, and 2 stands for a Li-vacancy in the [010] channel. 0 means Li-ion at Fe site. (b) The migration pathway of Li-ion diffusion predicted by our calculations. The yellow arrow represents the path of Li-ion hoping from the 1 site to the 2 site, which is along the [010] direction through face-shared vacant tetrahedral sites. The gray arrow represents the path of Li-ion hoping from the 0 site to the 2 site, which is along the [110] direction through face-shared vacant tetrahedral sites. (c) The energy barriers for a Li-ion to hop from the 1 site to the 2 site in the bulk Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 0$, 6.25\% and 12.5\%). IS, TS and FS represent the initial, transitional and final states, respectively.

![Figure 6](image6.png)

**Figure 6.** Full relaxed configuration for (a) LiFePO$_4$ and FePO$_4$; (b) Li$_{1.98}$Fe$_{1.02}$PO$_4$, Li$_{1.93}$Fe$_{1.07}$PO$_4$ and Fe$_{1.07}$PO$_4$. The unit of all bond lengths is Å.

![Table 2](image2.png)

**Table 2.** The calculated specific change of LiFePO$_4$ and Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$) during delithiation.

<table>
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<tr>
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<th>$\Delta a$ [Å]</th>
<th>$\Delta \sigma$ [Å]</th>
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<td>LiFePO$_4$</td>
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<td>0</td>
</tr>
<tr>
<td>FePO$_4$</td>
<td>4.36%</td>
<td>3.98%</td>
</tr>
</tbody>
</table>

This result is very close to 0.42 eV obtained by Christian Kuss.$^{51}$ In Li$_{1.98}$Fe$_{1.02}$PO$_4$ ($x = 6.25\%$ and 12.5\%), the barriers for a Li-ion to hop from the 1 site to the 2 site are 0.299 and 0.416 eV (Figure 7c), respectively, lower than the barrier of $x = 0$. This indicates that the excess Li-ions at Fe sites can enhance the Li-ion diffusivity along the adjacent [010] channel, coinciding with the results obtained by Kyu-Young Park.$^{39}$ The energy barriers for Li-ion diffusion along another adjacent [010] channel are shown in Figure S6, exhibiting the same inference. The enhanced Li-ion diffusivity in Li$_{1+x}$Fe$_{1-x}$PO$_4$ along the adjacent [010] channels can be explained as following: comparing...
the crystal structures of LiFePO$_4$ with Li$_{1+x}$Fe$_{1-x}$PO$_4$, the 0 site is occupied by Fe-ion in LiFePO$_4$, but is occupied by Li-ion in Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$ and $12.5\%$). Due to the much smaller charge of the Li-ion at Fe site, the Coulombic repulsion between the metal-ion at the 0 site and the Li-ion at the 1/2 site decreases greatly. In addition, the distance between the 1 site and the 2 site becomes shortened after Li-ions doping at Fe sites (Table S2).

Besides that, we calculated the diffusion barrier for a Li-ion hopping from the 0 site to the 2 site in the bulk Li$_{1+x}$Fe$_{1-x}$PO$_4$ ($x = 6.25\%$ and $12.5\%$). As shown in Figure 7d, the energy barriers are 0.707 and 0.834 eV, respectively, a little higher than the calculated result of the path 1-2, but much lower than 3.36 eV, which is the energy barrier for Li-ion diffusion along the [101] direction in the bulk LiFePO$_4$. GKP Dathar pointed that when Li-Fe anti-site defects arose in LiFePO$_4$, the energy barrier for a Li-ion to hop from the Fe site to the Li site in the adjacent [010] channel varied in the range of 0.75-0.85 eV. Malik et al. proved that Li-ion could cross over between different [010] channels and the diffusion mechanism tended to shift from 1D to 2D/3D in the presence of large concentration of anti-site defects. Therefore, we can see clearly that the Li-ion at the 0 site has the ability to transfer to the 2 site, activating the shift from 1D to 2D/3D diffusion. Figure 7b summarizes the migration pathway of Li-ion diffusion predicted by our calculations. Similar to migration pathway of Li-ion diffusion along the [010] channel (yellow arrow), Li-ion at Fe site hops from the Fe site to the Li site in the adjacent [010] channel via a tetrahedron hollow formed by the edge-sharing LiO$_6$ octahedra (gray arrow).

Conclusions
In summary, this work presents a systematic theoretical study of Li-rich olivine phase in LiFePO$_4$. Our calculated results show that Li$_{1+x}$Fe$_{1-x}$PO$_4$ are thermodynamically stable when $x$ does not exceed 12.5\%. Li$_{1+x}$Fe$_{1-x}$PO$_4$ cannot achieve the extra capacity by anionic redox activity, because the structure becomes unstable when the content of the extracted Li-ions exceeds (1-2$x$). This can be attributed to that the local oxygen-ion redox will cause the fracture of the rigid frame structure formed by phosphate tetrahedral polyanion. Though the extra capacity cannot be achieved in Li$_{1+x}$Fe$_{1-x}$PO$_4$, the ion diffusivity is enhanced by the excess Li-ions at Fe sites, reflected by the reduced energy barrier for the Li-ion diffusion along the adjacent [010] channel and the shift from 1D to 2D/3D diffusion. Our findings provide a fresh perspective on designing Li-rich cathode materials with high energy density.

Conflicts of interest
There are no conflicts to declare.

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Notes and references