Lithium Clustering during the Lithiation/Delithiation Process in LiFePO₄ Olivine-Structured Materials

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ABSTRACT: Olivine-structured LiFePO₄ is one of the most popular cathode materials in lithium-ion batteries (LIBs) for sustainable applications. Significant attention has been paid to investigating the dynamics of the lithiation/delithiation process in LiₓFePO₄ (0 ≤ x ≤ 1), which is crucial for the development of high-performance LiFePO₄ material. Various macroscopic models based on experimental evidence have been proposed to explain the mechanism of phase transition from LiFePO₄ to FePO₄, such as the shrinking core (i.e., core–shell) model, Laffont’s (i.e., new core–shell) model, domino-cascade model, phase transformation wave, solid solution model, many-particle models, etc. However, these models, unfortunately, contradict each other and their validity is still under debate. An atomistic model is urgently required to depict the lithiation/delithiation process in LiₓFePO₄. In this article, we reveal the lithiation/delithiation process in LiFePO₄ simulated by a computational model using the generalized gradient approximation (GGA + U) method. We find that the clustered configuration is the most energetically favorable, leading to co-operative Jahn–Teller distortion among the inter-polyhedrons that can be observed clearly from the bond patterns. This atomistic model not only offers answers to experimental results obtained at moderate or high rates but also gives the direction to further improve the rate capability of LiFePO₄ cathode material for high-power LIBs.

■ INTRODUCTION

Olivine-structured LiFePO₄ is fast gaining importance in today’s energy world, especially in high-power energy storage devices.¹⁻⁸ LiFePO₄ as a promising cathode material for high-power Li-ion batteries, compared with conventional lead–acid, nickel–cadmium, and even nickel–metal hydride batteries, are needed urgently to meet the demands of large-scale applications such as electric vehicles (EVs) and hybrid electric vehicles (HEVs).³,⁶ However, the mechanism of the phase transition from FePO₄ to LiFePO₄ is still under debate, which is believed to be crucial for the future development of high-performance LiFePO₄ materials.⁷,⁸ Along with essential demands to incorporate unique features, the understanding of the mechanism still attracts significant attention and leads scientists toward investigating the dynamics of the lithiation/delithiation process of LiₓFePO₄ (0 ≤ x ≤ 1), aiming at understanding the experimental results obtained at moderate or high rates and also giving directions to improve LiFePO₄ for high-power LIBs.⁹⁻¹¹

There are two phases of LiₓFePO₄ structures: the highly anisotropic fully lithiated LiₓFePO₄ (LFPO) and its delithiated counterpart, FePO₄ (FPO). The lithiation/delithiation process in LiₓFePO₄ (0 ≤ x ≤ 1) is commonly accepted as a two-phase reaction mechanism, with the movement of Li⁺ ions confined along the b-axis.¹² The pioneering work was carried out by Goodenough et al.,¹ who showed that the flat charge/discharge profile of LiFePO₄ arises from the motion of a two-phase interface. Recently, various macroscopic models based on experimental evidence have been proposed to explain the mechanism of phase transition from FePO₄ to LiFePO₄ such as the shrinking core (i.e., core–shell) model,¹³ Laffont’s (i.e., new core–shell) model,¹⁴ domino-cascade model,¹⁵ phase transformation wave,¹⁶ solid solution model,¹⁷ many-particle models,¹⁸ etc. All of these models intend to explain the lithiation/delithiation process in LiFePO₄ to help understand the experimental results. However, these models lack direct and convincing computational support. In this study, we use an atomistic approach to calculate the energy that it takes to incorporate Li⁺ ions into the FPO lattice. The method gives us an understanding of the lithiation and delithiation processes, which will be useful for future material development.

■ RESULTS AND DISCUSSION

Here, we use the first-principles density functional theory (DFT) GGA + U method to study the configuration of the lithium atoms because the method gives small error especially

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for transition metals with active localization of $d$ or $f$ orbitals compared with conventional GGA and linear discriminant analysis (LDA) methods.\textsuperscript{20−23} In the GGA + $U$ framework, the onsite Coulomb term $U$, and the exchange term $J$ can be merged into a single effective parameter $(U−J)$,\textsuperscript{37} and thus, we only need to take $U$ as an effective parameter that can be numerically fitted by a self-consistent ab initio calculation.\textsuperscript{25} For the olivine FePO$_4$ and LiFePO$_4$ system, the value of $U$ = 600 eV has been used as the cut-off energy for the atomistic simulation method.\textsuperscript{26} This value was first used the first-principles method and demonstrated that the diffusion coefficient $(D)$ along the [010] direction was several orders higher than that along the [001] direction. The result of $D$ (path $B$ [010])$/D$ (path $A$[010]) $\approx 10^{-37}$ showed that path B hardly made a contribution to the Li$^+$-ion motion, and the Li$^+$ ions diffused through one-dimensional (1D) channels along the [010] direction with a high energy barrier to cross between the channels. This large barrier was attributed to the FeO$_6$ octahedral transition state in path $B$ face-sharing two PO$_4$ tetrahedrons. Islam et al.\textsuperscript{35,38} furthermore modeled the structure of LiFePO$_4$ and investigated Li$^+$-ion migration energy in LiFePO$_4$ by the atomistic simulation method and found that Li$^+$ ion migration was preferential along [010] channels, following a curved trajectory. Li et al.\textsuperscript{39} studied the conductivity of Li$^+$ ions along the three principal directions of LiFePO$_4$ single crystals as a function of temperature (325−525 K) by AC impedance spectroscopy. Their results showed that Li$^+$-ion diffusion in LiFePO$_4$ is, to a large extent, confined to 1D through tunnels aligned along the $b$-axis. Furthermore, the experimental evidence of Li$^+$-ion diffusion along the [010] direction via PO$_4$ tetrahedral interstitial sites in Li$_{1-x}$FePO$_4$ ($x = 0.4$) was provided by combining high-temperature (620 K) powder neutron diffraction and the maximum entropy method.\textsuperscript{30} However, the mechanism of the phase transition from FePO$_4$ to LiFePO$_4$ is still under debate.\textsuperscript{9} When one lithium atom is inserted into the FePO$_4$ framework, the reaction energy is defined as below:

$$E_{\text{reac}} = E_{\text{Li}−\text{FPO}} − E_{\text{FPO}} − E_{\text{Li}}$$

Here, $E_{\text{LiFPO}}, E_{\text{FPO}},$ and $E_{\text{Li}}$ represent the total energy for the bulk LFPO, FPO, and bulk Li, respectively. For the second or third lithium inserted into the system, the corresponding $E_{\text{reac}}$ is defined similarly by replacing $E_{\text{FPO}}$ with the total energy before the lithium being inserted. This process is shown as step 4 of Path 1 in Figure 2. To further confirm the energy scale in this process, we compared the total energy gain of Path 2, which is about the direct combination of Li$^+$ and FPO$^-$ ions. Path 2 produced an energy difference of $\sim 11.7$ eV, which is very close to the summation of the energy of $\sim 11.67$ eV in all of the steps of Path 1.

As shown in Figure 3a, the first lithium inserts into a FePO$_4$ framework and is put in the center of the cell along the $b$-axis. An $E_{\text{reac}}$ value of $\sim −3.15$ eV was obtained, indicating that there is an energy favor of 3.15 eV after lithiation. The energy map for the third lithium insertion is shown in Figure 3b, and the optional positions for the second lithium insertion into FePO$_4$ are marked in Figure 3c. Each optional position for the second lithium has two choices along the $c$-axis, as shown by light green and light red balls in Figure 1b. However, we found that

### Table 1. Lattice Parameters and Band Gap values for FPO and LFPO with GGA + $U$ ($U = 4.3$) and Experimental (Exp) Values

|        | $a$ (Å) | $b$ (Å) | $c$ (Å) | gap (eV) |        | $a$ (Å) | $b$ (Å) | $c$ (Å) | gap (eV) |
|--------|---------|---------|---------|---------|--------|---------|---------|---------|---------|
| FPO    | 9.93    | 5.89    | 4.87    | 1.88    | FM     | 10.41   | 6.07    | 4.73    | 3.71    |
| AFM    | 9.93    | 5.88    | 4.86    | 2.07    | AFM    | 10.40   | 6.06    | 4.74    | 3.71    |
| exp$^{34}$ | 9.82    | 5.79    | 4.79    | N/A     | exp$^{34}$ | 10.06   | 5.89    | 4.64    | N/A     |

Figure 1. (a) Perspective view of the FePO$_4$ framework with one inserted Li$^+$-ion along the $b$-axis. The red, blue, and yellow sticks represent the FePO$_4$ units, and the green ball represents the Li$^+$-ion; the light green areas are the optional positions for nesting the second Li$^+$-ion. (b) Side view of the FePO$_4$ framework along the $c$-axis with two optional configurations marked by light green and pink balls.

The phosphorus atoms occupy tetrahedral sites forming PO$_4$ tetrahedrons with oxygen atoms. Iron atoms are on corner-sharing octahedral positions forming FeO$_6$ octahedrons, while lithium atoms occupy edge-sharing octahedral positions forming LiO$_6$ octahedrons. Each FeO$_6$ octahedron is linked with another four FeO$_6$ octahedrons through the shared corners in the $bc$ plane, forming inclined planes, parallel to the $c$-axis (i.e., [001] direction). The LiO$_6$ octahedrons form edge-sharing chains along the $b$-axis (i.e., [010] direction), creating Li tunnels along this direction. Each FeO$_6$ octahedron shares the edges with two LiO$_6$ octahedrons, while the PO$_4$ tetrahedron shares one edge with one FeO$_6$ octahedron and two edges with LiO$_6$ octahedrons, respectively.\textsuperscript{35,36} To study Li$^+$-ion transport in LiFePO$_4$, Morgan et al.\textsuperscript{37} used the first-principles method and demonstrated that the diffusion coefficient $(D)$ along the [010] direction was several orders higher than that along the [001] direction. The result of $D$ (path $B$ [010])/$D$ (path $A$[010]) $\approx 10^{-37}$ showed that path B hardly made a contribution to the Li$^+$-ion motion, and the Li$^+$ ions diffused through one-dimensional (1D) channels along the [010] direction with a high energy barrier to cross between the channels. This large barrier was attributed to the FeO$_6$ octahedral transition state in path $B$ face-sharing two PO$_4$ tetrahedrons. Islam et al.\textsuperscript{35,38} further modeled the structure of LiFePO$_4$ and investigated Li$^+$-ion migration energy in LiFePO$_4$ by the atomistic simulation method and found that Li$^+$ ion migration was preferential along [010] channels, following a curved trajectory. Li et al.\textsuperscript{39} studied the conductivity of Li$^+$ ions along the three principal directions of LiFePO$_4$ single crystals as a function of temperature (325−525 K) by AC impedance spectroscopy. Their results showed that Li$^+$-ion diffusion in LiFePO$_4$ is, to a large extent, confined to 1D through tunnels aligned along the $b$-axis. Furthermore, the experimental evidence of Li$^+$-ion diffusion along the [010] direction via PO$_4$ tetrahedral interstitial sites in Li$_{1-x}$FePO$_4$ ($x = 0.4$) was provided by combining high-temperature (620 K) powder neutron diffraction and the maximum entropy method.\textsuperscript{30} However, the mechanism of the phase transition from FePO$_4$ to LiFePO$_4$ is still under debate.\textsuperscript{9} When one lithium atom is inserted into the FePO$_4$ framework, the reaction energy is defined as below:

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the two configurations provide very similar results from the energy map (Supporting Information Figures S1–S3), and so here we only focus on the case as shown by the light green ball in Figure 1b.

For the second inserted lithium, the value of $E_{\text{reac}}$ generally increases when the distance between the two lithium ions increases. $E_{\text{reac}}$ is around $-3.48$ eV for the first nearest insertion positions as shown in Figure 3a (marked by blue triangles, corresponding to positions of a–f in Figure 3c), then increases above $-3.32$ eV for the second nearest insertion positions as shown in Figure 3b (marked by cyan triangles, corresponding to positions of g–j in Figure 3c), of which the distance is about 1 nm to the center lithium. For the farthest position k from the center (Figure 3c), the value of $E_{\text{reac}}$ is the highest, about $-3.17$ eV, which is very close to the $E_{\text{reac}}$ of the first lithium ($-3.15$ eV). The simulations indicate that the two Li+ ions prefer to form clusters rather than be far apart in the FePO$_4$ framework at low lithium concentration and there is little interaction between the two Li+ ions once the distance is larger than 1 nm.

When the third lithium is inserted, similar to the second lithium insertion case, $E_{\text{reac}}$ increases proportionally with the distance from the third lithium to the center lithium cluster, thus yielding a similar pattern. The favorable energy positions are a, b, and d, which are the nearest positions around the center lithium cluster. The $E_{\text{reac}}$ of position a is about $-3.58$ eV, which is a bit larger than that in the second lithium insertion case ($-3.48$ eV). Moreover, $E_{\text{reac}}$ of the clustering configuration (positions i, b, c, g, e, and f in Figure 3c) is about 200 meV energetic favorite than the far-separated positions (position k in Figure 3c). These results agree well with the previous two lithium cases, and the inserted third lithium prefers to form cluster states rather than the far-separated form. In 2006, Laffont et al. proposed a “new core–shell” model based on studies with high-resolution electron energy loss spectroscopy (HREELS). According to this model, Li+ migration along 1D channels is asynchronous. During charge, Li+ ions in the center of the platelet particles were extracted first and moved outward; whereas, during discharge, Li+ insertion started from the periphery. Their study unambiguously supports the view that the nanometer interfacial region consists of FePO$_4$ and LiFePO$_4$, but not solid solution Li$_x$FePO$_4$, which changes with the gradient of $x$ ranging from 0 to 1 by moving from FePO$_4$ to LiFePO$_4$. This two-phase mechanism attributed to the nature of the two phases. This Laffont’s new core–shell model accounts well for 1D migration, perpendicular to the platelets. A similar result was also observed by Chen et al. for the electron microscopy study of the LiFePO$_4$ to FePO$_4$ phase transition, indicating that the Li+ ions are extracted from narrow and disordered transition zones on the ac crystal plane as the phase boundary progresses in the direction along the a-axis. In 2008, Delmas et al. presented a “domino-cascade” model based on X-ray diffraction and electron microscopy technologies. This model agrees well with the HREELS study reported by Laffont et al., which shows that there is no solid solution Li$_x$FePO$_4$ in the interfacial region between the two limit compositions. According to this model, when the lithium insertion/extraction starts in a given particle, the particle rapidly becomes either charged or discharged. One essential difference between the new core–shell model and the domino-cascade model is the character of the interface. The former supports the coexistence of LiFePO$_4$ and FePO$_4$ regions inside each particle while the latter proposes the coexistence of LiFePO$_4$ and FePO$_4$ particles that are single-domain, indicating the clustering configurations of the lithium clusters in the FPO/LFPO phases. From Figure 3, we can see that the insertion energy lowers down with the increase of Li+ ion concentration, indicating that it is more likely for the Li+ ion to fill the FPO. In our simulation, $E_{\text{reac}}$ almost converged to zero when the

![Figure 3](https://example.com/figure3.png)

Figure 3. $E_{\text{reac}}$ energy map for (a) the second inserted lithium to the center of the lithium cluster, and (b) the third inserted lithium to the two lithium clusters. (c) Optional lithium insertion positions. The lithium atoms are marked as green balls, and the optional positions for the lithium are marked by small triangles. FePO$_4$ polyhedra is not shown for clarity.
lithium atoms are separated beyond 2 nm. Recently, some studies proposed that there was a solid solution zone during the charging/discharging process as a metastable process, which only lasts for hundreds of seconds and then turns into FPO/LFPO two phases. Another experiment observed the direct evolution of the phase transformation in individual LFPO nanoparticles during both slow and fast charge/discharge rates. The two experimental results provide solid support for our model, i.e., the clustering procedure leads the system to a clear final co-existing LFPO/FPO two-phase condition rather than a disorder solid solution, where the LFPO and FPO are randomly mixed.

Figure 4 shows the local bond patterns with 1, 2, and 3 Li+-ions inserted into the FPO framework based on the clustered configuration. For FeO$_6$ octahedrons, there are two kinds of Fe–O planar bond lengths, which are 2.16 and 2.07 Å (corresponding to $b_1$ and $b_2$ in Figure 4a, respectively). Due to symmetry, the values of $b_1$, $b_2$, $b_3$, $b_6$, $b_9$, and $b_{10}$ are equal, and the values of $b_4$, $b_5$, $b_7$, $b_8$, $b_{11}$, and $b_{12}$ are equal as well. Upon the insertion of one Li+-ion (Figure 4b), the Fe–O polyhedron is distorted and the bond length of $b_1$ to $b_4$ is increased by 0.3 Å due to the valence state change from Fe(III) to Fe(II). The distortion of the FeO$_6$ octahedron also leads to the rotation of the PO$_4$ tetrahedron with the bond lengths of $b_5$ and $b_6$ being reduced. Compared with FPO, the insertion of one Li atom leads to a total volume increase ($\Delta V_1$) of about 10 Å$^3$, while the total volume ($\Delta V_2$) increases by ca. 17 Å$^3$ after two Li$^+$ ions are inserted. The increased total volume is not in proportion to the number of Li$^+$-ions inserted ($\Delta V_2 < 2\Delta V_1$), indicating that there is a local structural distortion preventing further volume expansion. As shown in Figure 4c, when the second Li$^+$ ion is inserted, the bond lengths of $b_5$ to $b_{12}$ increase, but the bond lengths of $b_3$ and $b_9$ decrease by 0.2 Å due to the PO$_4$ tetrahedron rotation, which induces slight reduction of the bond lengths of $b_1$ and $b_2$. This kind of distortion belongs to the typical co-operative Jahn–Teller distortion, which is a local phase transition driven by the localized orbital electronic states. The clustered configuration of the Li$^+$ ions favors the co-operative Jahn–Teller distortion and results in the total energy minimization. For the third Li insertion with a clustered configuration (Figure 4d), the total volume ($\Delta V_3$) increases by 23 Å$^3$. Since $\Delta V_3 < \Delta V_1 + \Delta V_2 < 3\Delta V_1$, this again belongs to the co-operative Jahn–Teller distortion. Due to the insertion of more Li$^+$ ions, the fraction of Fe(III) is further reduced, and the Fe–O bond length increases in general. If there are more Li$^+$ ions, as shown by the white color in Figure 4d, there are more bonds with decreasing lengths, indicating that the co-operative Jahn–Teller distortion dominates this procedure for the clustering of the Li$^+$ ions during the lithiation process.

CONCLUSIONS

To summarize, by first-principles DFT calculation, we provide a clustering model to explain the lithiation/delithiation process with low lithium concentration in the FePO$_4$/LiFePO$_4$ structure. We find that the amount of volume expansion decreases when more lithium is inserted into the structure. From chemical bond patterns, one can see that the co-operative Jahn–Teller distortion is energetically favorable among the nearby FeO$_6$ octahedrons with the rotation of the PO$_4$ tetrahedron when the Li$^+$-ions are arranged in a clustered configuration. These results support that Li$^+$-ions prefer to form clusters rather than being far apart. Our result agrees well with the new core–shell model.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b02694.

Top and side views of the atomic structures; $E_{\text{rec}}$ energy map for the second and third inserted lithium atoms (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Padhi, A. K.; Nanjundaswamy, K. S.; Goodenough, J. B. Phospho-Olivines as Positive-Electrode Materials for Rechargeable Lithium Batteries. J. Electrochem. Soc. 1997, 144, 1188–1194.
(2) Padhi, A. K.; Nanjundaswamy, K. S.; Masquelier, C.; Okada, S.; Goodenough, J. B. Effect of Structure on the Fe3+/Fe2+ Redox Couple in Iron Phosphates. J. Electrochem. Soc. 1997, 144, 1609–1613.
(3) Chung, S. Y.; Bloking, J. T.; Chiang, Y. M. Electronically Conductive Phospho-Olivines as Lithium Storage Electrodes. Nat. Mater. 2002, 1, 123–128.
(4) Fergus, J. W. Recent Developments in Cathode Materials for Lithium Ion Batteries. J. Power Sources 2010, 195, 939–954.
(5) Tarascon, J. M.; Armand, M. Issues and Challenges Facing Rechargeable Lithium Batteries. Nature 2001, 414, 357–367.
(6) Marom, R.; Amalraj, S. F.; Leifer, N.; Jacob, D.; Aurbach, D. A. Review of Advanced and Practical Lithium Battery Materials. J. Mater. Chem. 2011, 21, 9938–9954.
(7) Yuan, L. X.; Wang, Z. H.; Zhang, W. X.; Hu, X. L.; Chen, J. T.; Huang, Y. H.; Goodenough, J. B. Development and Challenges of Lifepo4 Cathode Material for Lithium-Ion Batteries. Energy Environ. Sci. 2011, 4, 269–284.
(8) Wang, Y.; He, P.; Zhou, H. Olivine Lifepo4: Development and Future. Energy Environ. Sci. 2011, 4, 805–817.
(9) Malik, R.; Zhou, F.; Ceder, G. Kinetics of Non-Equilibrium Lithium Incorporation in Lifepo4. Nat. Mater. 2011, 10, 587–590.
(10) Bai, P.; Cogswell, D. A.; Bazant, M. Z. Suppression of Phase Separation in Lifepo4(4) Nanoparticles During Battery Discharge. Nano Lett. 2011, 11, 4890–4896.
(11) Hu, C. L.; Yi, H. H.; Fang, H. S.; Yang, B.; Yao, Y. C.; Ma, W. H.; Dai, Y. N. Suppressing Li3PO4 Impurity Formation in Lifepo4/Fe2p by a Nonstoichiometry Synthesis and Its Effect on Electrochemical Properties. Mater. Lett. 2011, 65, 1323–1326.
(12) Whittingham, M. S.; Song, Y. N.; Lutta, S.; Zavalij, P. Y.; Chernova, N. A. Some Transition Metal (Oxy)Phosphates and Vanadium Oxides for Lithium Batteries. J. Mater. Chem. 2005, 15, 3362–3379.
(13) Sinrivasan, V.; Newman, J. Discharge Model for the Lithium Iron-Phosphate Electrode. J. Electrochem. Soc. 2004, 151, A1517–A1529.
(14) Laffont, L.; Delacourt, C.; Gibot, P.; Wu, M. Y.; Kooyman, P.; Masquelier, C.; Tarascon, J. M. Study of the Lifepo4/Fepo4 Two-Phase System by High-Resolution Electron Energy Loss Spectroscopy. Chem. Mater. 2006, 18, 5520–5529.
(15) Delmas, C.; Maccario, M.; Croguennec, L.; Le Cras, F.; Weill, F. Lithium Deintercalation in Lifepo4 Nanoparticles Via a Domino-Cascade Model. Nat. Mater. 2008, 7, 665–671.
(16) Burch, D.; Singh, G.; Ceder, G.; Bazant, M. Z. Phase-Transformation Wave Dynamics in Lifepo4. In Theory, Modeling and Numerical Simulation of Multi-Physics Materials Behavior; Tikare, V.; Tikare, M. J.; Prieto, V. M. H.; Islam, M. S. Lithium Battery Materials Impedance (M = Mn, Fe, Co, and Ni): Insights into Defect Association, Transport Mechanisms, and Doping Behavior. Chem. Mater. 2008, 20, 5907–5915.
(17) Singh, G. K.; Ceder, G.; Bazant, M. Z. Intercalation Dynamics in Rechargeable Battery Materials: General Theory and Phase-Transformation Waves in Lifepo4. Electrochim. Acta 2008, 53, 7599–7613.
(18) Niu, J.; Kushima, A.; Qian, X.; Qi, L.; Xiang, K.; Chiang, Y.-M.; Li, J. In Situ Observation of Random Solid Solution Zone in Lifepo4 Electrode. Nano Lett. 2014, 14, 4005–4010.
(19) Dreyer, W.; Jammik, J.; Gubik, C.; Huth, R.; Moskow, J.; Gaberscek, M. The Thermodynamic Origin of Hysteresis in Insertion Batteries. Nat. Mater. 2010, 9, 448–453.
(20) Wang, L.; Maxisch, T.; Ceder, G. Oxidation Energies of Transition Metal Oxides within the Gga+U Framework. Phys. Rev. B 2006, 73, No. 195107.
(40) Nishimura, S. I.; Kobayashi, G.; Ohoyama, K.; Kanno, R.; Yashima, M.; Yamada, A. Experimental Visualization of Lithium Diffusion in \( \text{Li}_x\text{FePO}_4 \). Nat. Mater. **2008**, *7*, 707−711.

(41) Chen, G. Y.; Song, X. Y.; Richardson, T. J. Electron Microscopy Study of the \( \text{LiFePO}_4 \) to \( \text{FePO}_4 \) Phase Transition. Electrochem. Solid-State Lett. **2006**, *9*, A295−A298.

(42) Zhang, X.; van Hulzen, M.; Singh, D. P.; Brownrigg, A.; Wright, J. P.; van Dijk, N. H.; Wagemaker, M. Direct View on the Phase Evolution in Individual \( \text{LiFePO}_4 \) Nanoparticles During Li-Ion Battery Cycling. Nat. Commun. **2015**, *6*, No. 8333.

(43) Gehring, G. A.; Gehring, K. A. Co-Operative Jahn-Teller Effects. Rep. Prog. Phys. **1975**, *38*, 1.

(44) Zhou, F.; Cococcioni, M.; Marianetti, C. A.; Morgan, D.; Ceder, G. First-Principles Prediction of Redox Potentials in Transition-Metal Compounds with \( \text{Li}^{+}\text{U} \). Phys. Rev. B **2004**, *70*, No. 235121.