Anionic Redox Processes in Maricite- and Triphylite-NaFePO$_4$ of Sodium-Ion Batteries

Mei-ying Zheng, Zong-yao Bai, Yue-Wen He, Shunqing Wu,* Yong Yang, and Zi-Zhong Zhu*

ABSTRACT: In recent years, NaFePO$_4$ has been regarded as one of the most promising cathode materials for next-generation rechargeable sodium-ion batteries. There is significant interest in the redox processes of rechargeable batteries for high capacity applications. In this paper, the redox processes of triphylite-NaFePO$_4$ and maricite-NaFePO$_4$ materials have been analyzed based on first-principles calculations and analysis of Bader charges. Different from LiFePO$_4$, anionic (O$^{2-}$) redox reactions are evidently visible in NaFePO$_4$. Electronic structures and density of states are calculated to elaborate the charge transfer and redox reactions during the desodiation processes. Furthermore, we also calculate the formation energies of sodium and density of states are calculated to elaborate the charge transfer and redox reactions during the desodiation processes.

1. INTRODUCTION

In recent years, rechargeable lithium-ion batteries (LIBs) have been extensively used in electronic products, including smartphones, laptop computers, cameras, TVs, and other portable equipment. However, the development of LIBs is severely restricted by insufficient storage and uneven distribution of lithium in the earth’s crust. Currently, the cathode material used in LIBs is mainly the transition-metal oxide LiCoO$_2$, which contains the toxic and expensive cobalt element. Compared to LIBs, sodium-ion batteries (SIBs) are significantly cheaper since sodium materials are much more abundant on Earth, which makes SIBs more suitable for compact batteries and large-scale energy storage. While SIBs also face hurdles of an unsatisfying rate capability and limited cycling life caused by the relatively large radius and heavy mass of the Na$^+$ ion, layered transition-metal oxides of SIBs (NaMO$_2$, M = Co, Cr, etc.), as the first proposed cathode materials for SIBs, have attracted significant interest over the past decades. However, NaMO$_2$ electrode materials have a short life cycle and low thermal stability. Also, the complex reaction mechanisms of NaMO$_2$ usually result in multiple voltage plateaus during the charge–discharge processes. On the other hand, the phosphate polyanion family, including NaFePO$_4$, NaVPO$_4$, Na$_2$V$_2$(PO$_4$)$_3$, Na$_2$FePO$_4$, etc., seem to be promising candidates owing to the thermal stability and relatively high operating potentials. The electrochemical performances of different types of cathode materials for SIBs are listed in Table 1. Among various cathode materials listed, triphylite- and maricite-NaFePO$_4$ show the highest practical capacities, although the layered transition-metal oxides O$_3$-NaFeO$_2$ and P$_2$-NaCoO$_2$ have the highest theoretical capacities. For all the materials in Table 1, the average voltages are approximately 3.0 V, expect that Na$_2$FeSiO$_4$ has a low average voltage of approximately 1.9 V and Na$_2$CoPO$_4$F a high voltage of approximately 4.3 V. In addition, both the

<table>
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<th>Cathode Material</th>
<th>Theoretical/Practical Capacity (mAh/g)</th>
<th>Average Voltage</th>
<th>Capacity Retention (%)</th>
<th>Ref.</th>
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<td>0.5 C, 70% (200 cycles)</td>
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<tr>
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<td>3.0 V</td>
<td>1 C, 80% (200 cycles)</td>
<td>14</td>
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<tr>
<td>Na$_2$FeSiO$_4$</td>
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<td>200 mA/g, 94% (20 cycles)</td>
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<td>61 mA/g, 37.4% (20 cycles)</td>
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Received: December 9, 2019
Accepted: February 12, 2020
Published: March 4, 2020
triphylite- and maricite-NaFePO₄ have good capacity retentions, as compared to other materials in Table 1. In comparison with classical cathode-material LiFePO₄, NaFePO₄ in SIBs, as the sodium analogue of LiFePO₄, has the highest theoretical capacity of 155 mA h/g among the phosphate polyanion cathode materials.¹⁷⁻²⁰ Meanwhile, iron-based sodium phosphates are cost-effective and environmentally friendly.²¹ Unlike LiFePO₄, the NaFePO₄ analogue exists in two distinct polymorphs (triphylite and maricite). Triphylite-NaFePO₄ is isostructural to LiFePO₄ and offers a one-dimensional channel delivering a reversible discharge capacity exceeding 120 mA h/g.²² However, triphylite-NaFePO₄ is not the thermodynamically stable phase and usually obtained from olivine-LiFePO₄ through complicated ion exchange processes.²² Maricite-NaFePO₄ can be synthesized by a simple solid-state method and is the thermodynamically stable phase.²³,²⁴ While the thermodynamically favored maricite-NaFePO₄ is commonly considered as electrochemically inactive due to the lack of Na⁺ ion diffusion channels.²³,²⁴,²⁵ However, by reducing dimensions of NaFePO₄ to the nanoscale and introducing a carbon matrix, maricite-NaFePO₄ may show admirable electrochemical performance (145 and 60 mA h/g at 0.2 and 50 C).²¹

Redox processes in LIBs/SIBs is under hot discussion. In many cases, both the transition metals and anions may participate in the charge compensation during the charging/discharging processes. For reaching higher capacities, one possibility is to utilize oxygen/sulfur redox.²⁶ Therefore, the loss of charge in O²⁻ (redox) becomes an important aspect for studying the high capacity of LIB/SIB electrode materials. In recent reports, combined experimental and theoretical studies of O²⁻ redox processes have been reviewed.²⁷ Tarascon’s group demonstrated that the redox activity of oxygen is responsible for the extra capacity in Na₂Ru₀.₇₅Sn₀.₂₅O₃.²₈ Ke Du and co-workers reported that Na₀.₆[Li₀.₂Mn₀.₈]O₂ shows a high reversible capacity contributed by the oxygen redox.²⁹ Recent extensive research work has demonstrated that oxygen anions do participate in the charge compensation in addition to the cationic redox reactions and investigated anionic redox activities also widely in the research field for new high-capacity electrodes.²⁶,³⁰⁻³⁵ However, as of today, Bader charge calculations and analysis of charge transfer in NaFePO₄ has not yet been well studied. In this paper, we analyze the Bader charge during the desodiation processes in order to understand the redox reaction processes in both maricite-NaFePO₄ and triphylite-NaFePO₄. In LiFePO₄, charge compensation is only dominated by cationic Fe³⁺. Thus, an anionic redox reaction may not expected in NaFePO₄, which has neither abundance of oxygens nor deficiency of transition-metal cations. However, one of the significant contribution of this work is that we find that visible anionic (O²⁻) redox processes exist in NaFePO₄ systems, which is different from LiFePO₄. Additionally, electronic structures and density of states are calculated to elaborate the charge transfer and redox reactions. We also calculated the voltages, crystal volume changes, deformation charge densities, and the magnetization during the desodiation processes to help understand the electrochemical properties involved.

2. RESULTS AND DISCUSSION

Sodium iron phosphate (NaFePO₄) has two morphologies, that is, triphylite-NaFePO₄ and maricite-NaFePO₄. Both NaFePO₄ morphologies crystallize in the orthorhombic structure with the space group Pnma.²⁰,³⁶ Each unit cell contains four formula units (f.u.), that is, 4 sodium, 4 iron, 4 phosphorus, and 16 oxygen atoms, as shown in Figure 1. By using the DFT calculations, the structural parameters of NaFePO₄ are found to be a = 4.996 Å, b = 6.267 Å, and c = 10.483 Å for triphylite-NaFePO₄ and a = 5.087 Å, b = 6.883 Å, and c = 9.102 Å for maricite-NaFePO₄, being in excellent agreement with the experimental values in a deviation of only 1% (see Table 2). In order to simulate the desodiation processes, supercells are constructed with the unit cell vectors expanded triple times along the a, b and c directions. Finally, supercells adopted for the present calculations contain 12 formula units of NaFePO₄, which is 84 atoms/supercell.

In each Na₁₋ₓFePO₄ₓ sample, x represents the number of extracted sodium ions in the supercells. Although the maricite phase has the same anionic framework as the triphylite phase, the structural disparity between triphylite- and maricite-NaFePO₄ is noticeable. To be more specific, Na⁺ occupied the 4a location and Fe²⁺ occupied the 4c location in triphylite-NaFePO₄. In contrast, for maricite-NaFePO₄, 4a and 4c cation-site occupations are completely reversed, that is, Fe²⁺ occupied all 4a sites while Na⁺ occupied the 4c location. In triphylite-NaFePO₄ (Figure 1a), the PO₄ tetrahedron and FeO₆ octahedron form a structure sharing two oxygen atoms accommodated in the same edge. Analogous to triphylite-LiFePO₄, this type of structure provides a migration path for Na⁺ along the b direction, which is vital for
intercalation and deintercalation of sodium. In maricite-NaFePO$_4$ (Figure 1b), two adjacent FeO$_6$ octahedra share edges and form a FeO$_6$ chain. One PO$_4$ tetrahedron connects three parallel FeO$_6$ chains, which is a major impediment to the migration of sodium ions along the $b$ direction. Therefore, maricite-NaFePO$_4$ is usually considered as an electrochemically inactive material on account of lacking feasible diffusion pathways of sodium ions. However, Kim et al. reported that maricite-NaFePO$_4$ can also act as an excellent cathode material for rechargeable sodium batteries since the sodium extraction/insertion could be reversible in nanoscale maricite-NaFePO$_4$.

To study the charging/discharging processes as well as the structural evolution of the Na$_{1-x}$FePO$_4$ crystal, Na ions are removed one by one in the supercell ($x = 1, 2, 3, ..., 12$) from the relaxed structures (see Figure 1). In order to search for the most stable structure at each configuration in the Na$_{1-x}$FePO$_4$ system, 5018 structures ($2[C_{12}^{1} + C_{12}^{2} + C_{12}^{3} + C_{12}^{4}]$) should be taken into consideration. Actually, we need only to calculate about 230 different configurations by considering symmetry operations on the 5018 structures. Figure 2 plots the formation energies per formula for triphylite-NaFePO$_4$. The formation energy in NaFePO$_4$ can be calculated by the following formula

$$E_f = E(Na_{1-x/12}FePO_4) - (1 - x/12)E(NaFePO_4)$$

where $E$ represents the total DFT cohesive energy per formula unit and $x$ represents the number of removed sodium ions in the supercell. We build up the corresponding convex hull based on the DFT formation energies as a function of the Na
is the atomic position. The contour plots of the formula for the average voltage during Na-ion extraction from ag agreement with the results calculated by Saracibar et al.\textsuperscript{39} for the redox compensation. dashed line represents the corresponding theoretical values required charges for triphylite- and maricite-structures, respectively. The sodium compositions. The blue and red lines represent total Bader minimal energy are de\textsuperscript{f}i\textsuperscript{e}xtracted amount. Vertices of the convex hull representing the minimal energy are defined as ground states at each composition. Thus, these minimal energy structures are considered to be stable intermediate phases that can be generated during the charging and discharging cycles. Shown in Figure 2a, there are two ground states existing at $x = 2$ and $x = 4$ of triphylite-Na$_{1-x/12}$FePO$_4$, indicating that two stable intermediate phases Na$_{0.83}$FePO$_4$ and Na$_{0.67}$FePO$_4$ can be observed in the charge processes, which is in excellent agreement with the results calculated by Saracibar et al.\textsuperscript{39} Based on the above convex hull, the average charging voltages for the triphylite-NaFePO$_4$ systems are computed. The formula for the average voltage during Na-ion extraction from NaFePO$_4$ systems is as follows

$$U = \frac{E(Na_{1-x_{Na}}\text{Host}) - E(Na_{1-x_{Na}}\text{Host}) + (x_1 - x_2)E(Na)}{(x_1 - x_2)\epsilon}$$

where $x_1$ and $x_2$ are the Na compositions before and after sodium extraction in the host, respectively. $E(Na_{1-x_{Na}}\text{Host})$ and $E(Na_{1-x_{Na}}\text{Host})$ are the total cohesive energies of the systems before and after desodiation. $E(Na)$ is the energy of a single sodium atom. Two stable phases in Figure 2a lead to three voltage plateaus during the desodiation processes in Na$_{1-x/12}$FePO$_4$ systems, as shown in Figure 2b. The first plateau of the voltage is 2.83 V corresponding to $x = 0$–2, the second voltage is 2.96 V corresponding to $x = 2$–4, and finally, it is increased to 3.12 V upon full desodiation. It is worth noting that the simulated voltage plateaus of NaFePO$_4$ are in reasonable agreement with the experimental GITT (i.e., galvanostatic intermittent titration technique), which shows two voltage plateaus of $\sim$2.89 and $\sim$3.06 V. However, the GITT does not show the specific voltage plateau around $x = 2$, which might be due to the smaller formation energy of the Na$_{0.83}$FePO$_4$ phase compared with NaFePO$_4$ and Na$_{0.67}$FePO$_4$ phase reported by Saracibar et al.\textsuperscript{39}

Volume changes play an indispensable role during the electrochemical cycling. Figure 3 shows the corresponding changes of the unit cell volume at various Na compositions for maricite-NaFePO$_4$ and triphylite-NaFePO$_4$. The full-desodiated phase leads to a volume contraction of 14.45 and 12.54% for maricite-NaFePO$_4$ and triphylite-NaFePO$_4$, respectively, which are relatively too large for the application of NaFePO$_4$ in sodium batteries. Also, these volume changes are larger than those of LiFePO$_4$ ($\sim$7\%).\textsuperscript{40} The volume decrease of maricite-NaFePO$_4$ is always a little bit larger than that of the triphylite system. Generally speaking, Na$_{1-x/12}$FePO$_4$ could be an acceptable cathode material for sodium batteries when $x < 8$.

In order to further understand the bonding properties of NaFePO$_4$ and the influence of atomic bonding on the redox processes, we calculated the deformation charge densities on some important surfaces based on the optimized structures. Herein, the deformation charge density is defined as the difference between the total charge density of the self-consistent system $\rho(\tilde{r})$ and the superposition of the individual atomic charge density, that is

$$\Delta \rho(\tilde{r}) = \rho(\tilde{r}) - \sum_{\mu} \rho_{\mu}^{\text{atom}}(\tilde{r} - \tilde{R}_{\mu})$$

where $\tilde{R}_{\mu}$ is the atomic position. The contour plots of the deformation charge densities, as given in Figure 4, can clearly visualize the charge transfer between atoms, which can help us analyze the bonding characteristics of the materials.\textsuperscript{41,42} The solid lines in the figure represent the accumulation of charge relative to independent atoms, while the dashed lines depict the area with loss of charge. In both the maricite and triphylite-NaFePO$_4$ systems, P–O and Fe–O bonds exhibit strong covalent and ionic characteristics simultaneously. Figure 4a shows the deformation charge density of the plane that contains two oxygen atoms surrounding a central phosphorus atom in a PO$_4$ tetrahedron of maricite-NaFePO$_4$. PO$_4$ always forms a compact tetrahedron, which is composed of very strong P–O covalent bonds. The situation is similar in triphylite-NaFePO$_4$ where compact PO$_4$ also exists. In this case, the deformation charge density of the PO$_4$ tetrahedron in triphylite-NaFePO$_4$ will not be shown. In Figure 4b, not only P–O bonds are displayed but also the charge surrounding sodium ion is exhibited for maricite-NaFePO$_4$. It can be seen that sodium loses all its valence electrons and becomes an

Figure 5. Bader charges of triphylite-NaFePO$_4$ and maricite-NaFePO$_4$ during the Na-ion extraction. The blue and red lines represent Bader charges for triphylite- and maricite-systems, respectively.

Figure 6. Sum of Bader charges from Fe, P, and O ions at different sodium compositions. The blue and red lines represent total Bader charges for triphylite- and maricite-structures, respectively. The dashed line represents the corresponding theoretical values required for the redox compensation.
isolated Na$^+$ ion. Considering the great differences of Fe–O bonds in maricite-NaFePO$_4$ and triphylite-NaFePO$_4$, we discuss in more detail the deformation charge densities of Fe–O bonds. In maricite-NaFePO$_4$ (Figure 4c), all the six O ions in octahedral FeO$_6$ share the vertex positions with the surrounding six PO$_4$ tetrahedra. Therefore, as shown in Figure 4c, the four Fe–O bonds are quite similar, and the angles of O–Fe–O are all close to 90$^\circ$. In triphylite-NaFePO$_4$, on the other hand, two oxygen atoms (i.e., O1 and O2, see Figure 4d) in the FeO$_6$ octahedra share an edge of a PO$_4$ tetrahedron. From Figure 4d, we can see that the bond angles of O–Fe–O differ significantly, leading to a smaller O–Fe–O angle for oxygen atoms with edge sharing and large O–Fe–O angles for the oxygen atoms without edge sharing. Comparing Figure 4c with Figure 4d where the charge density plot is presented, we can see that the Fe–O1 bonding in triphylite is stronger than Fe–O1 bonding in maricite, both covalently and ionically indicated by a larger charge loss (dashed line) around Fe and much shorter bond length between Fe–O1 (2.09 Å compared with 2.39 Å) in triphylite.

In order to understand the anionic redox processes in NaFePO$_4$ of sodium-ion batteries, the Bader charges are calculated by first-principles calculations. The loss of Bader charge relative to that of the full-sodiated phase ($x = 0$) is shown in Figure 5 as a function of the composition $x$ in Na$_{1-x/12}$FePO$_4$. As shown in Figure 5, redox processes are always dominated by iron ions both in maricite-NaFePO$_4$ and triphylite-NaFePO$_4$ systems. It is worth noting that the redox processes of oxygen are also obvious during the desodiation processes since the loss of charge for O is clearly visible. However, the loss of charge from P is inconspicuous along $x = 0$ to $x = 12$ in consistency with the strong electronegativity and difficulty to lose electrons of P ions. Compared with the well-studied LiFePO$_4$, the situation for NaFePO$_4$ is significantly different. It is well known that, in LiFePO$_4$, only Fe$^{2+}$ participates in the charge compensation because the energy levels of oxygen ions are buried deep below the Fermi level; hence, oxygen atoms are hardly excited. Therefore, the lithium iron phosphate material does not exhibit anion redox. However, in both triphylite- and maricite-NaFePO$_4$, the energy levels (see DOS plots below) of oxygen ions are located near or cross the Fermi surfaces during the desodiation processes. Such participation of oxygen ions with the changes of electronic structures during the desodiation processes results in visible anionic redox processes in NaFePO$_4$, which is apparently different from the LiFePO$_4$ system. At each composition $x$, the total Bader charge per formula unit relative to the full-sodiated state during the redox processes is shown by solid lines in Figure 6. Once Na$^+$ is removed, the remaining ions (Fe, P, and O ions) have to contribute one electron in order to accomplish charge compensation. The dashed line in Figure 6 represents the amount of electrons required to compensate for the charge loss during the sodium removal processes. Therefore, the deviation between the solid and dashed lines indicates the inaccuracy of the Bader charge calculation method.
To further understand the redox processes in Na$_{1-x}$$\text{FePO}_4$, we present in Figure 7 the spin-polarized partial density of states (PDOS) of the Fe 3d, O 2p, and P 3p states at $x=0, 6, 12$ for the triphylite system. The calculated electronic structures suggest that the full-sodiated phase ($x=0$) and full-desodiated phase ($x=12$) are semiconductors with moderately large gaps of 3.54 and 1.66 eV, respectively, while the intermediate phase ($x=6$) is metallic. The large band gap demonstrates poor electronic conductivity existing in NaFe-PO$_4$, which can be resolved by carbon coating and low-temperature synthesis routes.\textsuperscript{44} At $x=0$ (Figure 7a), we find that there are two noticeable peaks near/below the Fermi surface in the PDOS plot. Although the peak of Fe is significantly larger than that of oxygen, however, the peak of oxygen is still visible. When sodium ions were began to be removed, the electrons on these two peaks will be oxidized at first. Such a picture is capable of explaining the loss of electrons not only in Fe prominently but also in O visibly.

Figure 8. Partial density of states of maricite-Na$_{1-x}$$\text{FePO}_4$ for (a) $x=0$, (b) $x=1$, (c) $x=11$, and (d) $x=12$. The Fermi level is set at 0 eV.

Figure 9. (a) Spin-down band structures of maricite-Na$_{1-x}$$\text{FePO}_4$ ($x=11$) where the dot-dashed line indicates the location of the Fermi level. (b) Atomic orbital contributions of Fe 3d and O 2p are shown as pink translucent circles and blue dots, respectively.

\textsuperscript{44} ACS Omega 2020, 5, 5192–5201
during the initial redox processes. At the intermediate phase of $x = 6$ (Figure 7b), the dominant peak of Fe 3d and the relatively weak peak of O 2p appear around the Fermi surface. Upon further desodiation, electrons on the peaks at the Fermi surface will lose. The electronic states on the Fermi surface again explain the redox behavior of both Fe and O (see Figure 5). Overall, from both $x = 0$ and $x = 6$, we see that both Fe and O ions participate in the redox processes in which electron loss of Fe is striking while the anionic redox (electron loss of O) is also noticeable. For the maricite system, the spin-polarized partial density of states (PDOS) of Fe 3d, O 2p, and P 3p states are shown in Figure 8. The PDOS calculations suggest that the systems with $x = 0, 11, 12$ are all semiconductors with gaps of 3.69, 0.30, and 1.65 eV, respectively. While Na$_{0.08}$FePO$_4$ ($x = 2$) is metallic. Similar to the cases in triphylite-NaFePO$_4$, noticeable peaks of PDOS at the Fermi surface are found for both $x = 0$ and 1 (Figure 8a,b) where the peaks of Fe 3d are significantly larger than those of O 2p. The peaks of oxygen at the Fermi surface indicate that oxygen ions also participate in the initial redox process. The calculated spin-down band structures corresponding to $x = 11$ are shown in Figure 9a, helping us understand the contribution of electronic orbitals to the electrons near the Fermi surface. The Na$_{0.08}$FePO$_4$ ($x = 11$) is a direct gap material. We zoom the two bands around the Fermi level in Figure 9a and show them in Figure 9b. The translucent circles and the dots represent the contribution of Fe 3d and O 2p to the band, respectively. Although Fe plays a critical role near the Fermi surface, oxygen still accounts for a visible proportion, which illustrates the presence of the anionic redox.

Summarizing, for both the triphylite and maricite systems, we can hardly see the P 3p peaks in the PDOS plots during the whole desodiation processes, suggesting that P scarcely participates in the redox processes. The PDOS plots also indicate that oxygen ions are clearly spin-polarized in the NaFePO$_4$ systems for all the compositions of $x$, although O usually does not show spin polarization. For a wide energy range in PDOS plots, for example, from $-5$ to 0 eV, peaks of Fe 3d and O 2p show significant overlaps, indicating that Fe and O orbitals possess strong hybridization. Such an effect of strong hybridization makes the energy levels of oxygen pushed to cross the Fermi surface, which explains the reason why oxygen ions are capable of participating in the anionic redox processes in the systems studied.

It is widely known that lithium ions diffuse along the [010] channel in LiFePO$_4$. Similar migration trajectories exist in triphylite-NaFePO$_4$, Figure 10a shows the migration pathway of Na-ion diffusion along the $b$ direction. The energy barrier along this path is 0.35 eV as shown in Figure 10b, which is in consistency with previously reported values. Compared with LiFePO$_4$, the energy barrier for Na diffusion in triphylite-
NaFePO$_4$ is slightly higher (0.29 eV in LiFePO$_4$). Diffusions along other directions in triphylite-NaFePO$_4$ and all the directions in maricite-NaFePO$_4$ are difficult since the migration paths are blocked by polyhedra. For a given FeO$_6$ octahedron, the five 3d orbitals of Fe split into two sets with $e_g$ (double-degenerate $d_{xy}$ and $d_{xz}$, $d_{yz}$) orbitals and $t_{2g}$ (triple-degenerate $d_{x^2-y^2}$, $d_{xy}$, and $d_{yz}$) orbitals. Symmetries. The energy levels of orbitals in a $t_{2g}$ symmetry are comparatively lower than those of $e_g$. Under the ligand field of sodium iron phosphate, the $d_{x^2-y^2}$, $d_{xy}$, and $d_{yz}$ atomic orbitals of Fe (the $t_{2g}$ set) are nonbonding, while the $d_{xy}$ and $d_{yz}$ atomic orbitals possess both bonding ($e_g$) and anti-bonding ($e_g$) states. The electronic configuration of Fe atom is $3d^64s^2$, and Fe atoms will lose their two 4s electrons in the processes of forming NaFePO$_4$. 3d electrons of Fe ions will arrange in a high-spin state (HS state). Specifically, five d electrons in the 3d orbital of Fe$^{3+}$ (3d$^6$) will occupy the five spin-up energy levels in both the $t_{2g}$ and $e_g$ bands, while the remaining single d electron occupies a spin-down energy level in the $t_{2g}$ band, leading to the total magnetization of 4 $\mu_B$/atom. The spin-down levels are higher than all the five spin-up levels, as shown in Figure 11a. When Na$^+$ is extracted, Fe$^{2+}$ participates in the redox process, which means that Fe$^{3+}$ ions are oxidized to Fe$^{3+}$ ions. The spin-down electron accommodated in the triple-degenerate $t_{2g}$ bands that are close to the Fermi level will be lost. The remaining five electrons in the 3d orbital of Fe$^{3+}$ still occupy all the spin-up energy levels, leading to the magnetization of 5 $\mu_B$/atom. The calculated magnetic moments of NaFePO$_4$ ($x = 0$ and Fe$^{3+}$) and FePO$_4$ ($x = 12$ and Fe$^{3+}$) are 3.78 and 4.33 $\mu_B$, respectively, which agree well with our theoretical analysis of magnetic moments. The magnetic moment of iron increases linearly with the sodium removal processes for both triphylite-NaFePO$_4$ and maricite-NaFePO$_4$. The magnetization of Fe$^{3+}$ to Fe$^{3+}$ during sodium extraction seems to be independent for different Fe ions, which explains the linear behavior of magnetization in Figure 11b.

3. CONCLUSIONS

Anionic redox may provide a larger capacity for rechargeable batteries, therefore, the investigation of redox reactions is of great significance. In this paper, the anionic redox processes of both triphylite-NaFePO$_4$ and maricite-NaFePO$_4$ systems have been depicted by first-principles calculations of Bader charges. Analysis on the Bader charge are performed to account for the anionic (O$^{2-}$) redox processes during the desodiation processes. Results show that the loss of charge for O ions are noticeable during the entire desodiation processes in NaFePO$_4$, which is quite different from LiFePO$_4$ where the loss of charge for O ions is negligible. However, the decrease of Bader charges on oxygen ions in all the cases is less than 0.1e/ oxygen, which indicates a “weak” anionic redox reaction in NaFePO$_4$. The role of the anionic redox reaction in the high capacity of NaFePO$_4$ is also weak. The electronic density of states is also calculated to elaborate the charge transfer and redox reactions. Additionally, the formation energies and convex hull are calculated to construct the average voltage plateaus, which show three voltage plateaus with different sodium compositions. The deformation charge densities and magnetization for NaFePO$_4$ have also been discussed to help us understand the redox reactions.

4. COMPUTATIONAL METHODS

The present calculations on the anionic redox processes were performed by using a first-principles method based on the density functional theory (DFT), as implemented in the Vienna ab initio simulation package (VASP). The VASP is based on the plane-wave basis and the projector augmented wave (PAW) representation. The Perdew–Burke–Ernzerhof (PBE) exchange-correlation energy functional within the generalized gradient approximation (GGA) is employed in the calculations. To address the on-site Coulombic interactions in the localized d electrons of Fe ions, the GGA + U method with an additional Hubbard-type U term (U eff = U – J; J = 5.3 eV, J = 1 eV for Fe) is applied. The wave functions are expanded in a plane-wave basis up to a kinetic energy cutoff of 600 eV. The convergence of the total binding energy of the system with respect to the plane-wave kinetic energy cutoff has been tested. Brillouin-zone integrations were performed by using k-point sampling mesh generated according to the Monkhorst-Pack method. The atomic coordinates in the unit cell are fully relaxed in each system until the forces on all the atoms are smaller than 0.01 eV/Å. Since the magnetic properties of Fe atoms may have important influences on the properties of the electronic structures of the materials, spin-polarized calculations are performed for all the systems. In order to address reasonably the charge transfer between the ions, which is closely related to the redox processes in the systems, the detailed exploration about charge transfer between atoms was made by the analysis of the calculated Bader charges.

AUTHOR INFORMATION

Corresponding Authors
Shunqing Wu — Department of Physics, OSED, Key Laboratory of Low Dimensional Condensed Matter Physics (Department of Education of Fujian Province), Xiamen University, Xiamen 361005, China; orcid.org/0000-0002-2545-0054; Email: wsq@xmu.edu.cn

Zi-Zhong Zhu — Department of Physics, OSED, Key Laboratory of Low Dimensional Condensed Matter Physics (Department of Education of Fujian Province) and Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen University, Xiamen 361005, China; orcid.org/0000-0001-5353-4418; Email: zzhu@xmu.edu.cn

Authors
Mei-ying Zheng — Department of Physics, OSED, Key Laboratory of Low Dimensional Condensed Matter Physics (Department of Education of Fujian Province), Xiamen University, Xiamen 361005, China

Zong-yao Bai — Department of Physics, OSED, Key Laboratory of Low Dimensional Condensed Matter Physics (Department of Education of Fujian Province) and Fujian Provincial Key Laboratory of Theoretical and Computational Chemistry, Xiamen University, Xiamen 361005, China

Yue-Wen He — Department of Physics, OSED, Key Laboratory of Low Dimensional Condensed Matter Physics (Department of Education of Fujian Province), Xiamen University, Xiamen 361005, China

Yong Yang — State Key Lab for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China; orcid.org/0000-0003-1145-8992

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b04213
ACKNOWLEDGMENTS

This work is supported by the National Key R&D Program of China (nos. 2016YFB0901502 and 2016YFA0202601) and National Natural Science Foundation of China (nos. 21761132030 and 11874307).

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