Dynamic Lithium Intercalation/Deintercalation in 18650 Lithium Ion Battery by Time-Resolved High Energy Synchrotron X-Ray Diffraction

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A time-resolved in situ high energy synchrotron X-ray diffraction (HESXRD) technique is employed to study the lithiation/delithiation of cathode/anode in a commercial 18650 battery under real working condition (current rate is 4 C). The phases and their changes in both the cathode and anode are identified simultaneously. For the anode component, during the charge process, as well as the Li$_x$C$_6$ phase, a lithium-rich phase close to LiC$_6$ phase and a series of intermediate phases between the Li$_x$C$_6$ and LiC$_6$ phases are observed. A distinct lithium intercalation/deintercalation mechanism is proposed for the cathode. The transforms of LiFePO$_4$ into the FePO$_4$ consists three periods with different components of phases, i.e., LiFePO$_4$ + lithium-deficient solid solution phases (period I), FePO$_4$ + LiFePO$_4$ phases (period II), and FePO$_4$ + lithium-rich solid solution phases (period III). The changes in both the anode and cathode during the discharge process are just inversed to those occurs during the charge process. The present work indicates that dynamic lithiation/delithiation process under real working condition is different from those at the thermodynamic state, and the in situ HESXRD is one of the most promising technique to monitor such kind of dynamic lithium behavior.

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In the past twenty years, lithium ion battery experienced a fast development due to its large energy density, high voltage and excellent cycle performance.1-2 While various Li ion battery systems are commercialized, the understanding of the lithiation/delithiation process mechanism occurred in electrode material is recognized to be crucial in developing new batteries and thus is attracting more and more attentions. To study the structure changes in electrode materials during lithium intercalation/deintercalation, various of in situ techniques, such as X-ray diffraction (XRD),3-5 X-ray absorption,6-7 Raman spectroscopy,8 nuclear magnetic resonance9-10 and transmission electron microscopy,11 have been employed. However, these techniques possess a weak ability of penetration and can be only utilized in the characterization of some special designed batteries.12-14 Besides, most of these techniques are based on step-scan mode, by which as long as several minutes are usually required to collect the structure information. Therefore, a small current density has to be applied in order to monitor effectively the structure change in electrode materials. The thus-obtained mechanisms disclosed only the lithiation/delithiation process under thermo-dynamic equilibrium status.15-16 In addition, in the graphite/LiFePO$_4$ battery system, while the intercalation/deintercalation mechanism on the anode (graphite/Li$_x$C$_6$) has been well established, that on the cathode (FePO$_4$/LiFePO$_4$) is still under debate.17-19 It was usually reported in the literature that the lithiation/delithiation of FePO$_4$/LiFePO$_4$ involved either a two-phase reaction18-19 or a solid-solution reaction.20-22 However, notwithstanding the differences in these mechanisms, they both reflect the lithium behaviors during the thermodynamic equilibrium process, due to the employment of conventional characterization techniques mentioned as above. Recently, some researchers also proposed that the solid-solution and two-phase reactions occurred concurrently during the charge/discharge processes under dynamic conditions.23 Therefore, the clarification of the mechanism for the lithiation/delithiation in FePO$_4$/LiFePO$_4$ is highly desired, and this is apparently dependent on the employment of efficient characterization techniques that are able to monitor the lithium behavior in the dynamic process under real working condition.

Due to the large penetration depth of neutrons in comparison to the lab X-rays used in traditional XRD, in situ neutron diffraction/scattering was employed to study the lithium intercalation/deintercalation process in a commercial prismatic lithium ion battery.24-26 However, this technique is associated with a major drawback that neutrons can react with hydrogen, which is abundant in the electrolyte in a lithium ion battery, to generate a large scattering cross-section and thus very strong background, reducing largely the signal/noise ratio of diffraction peaks. Recently, high energy synchrotron X-ray diffraction (HESXRD) is recognized to be a promising tool in the studies of structural phase-transitions in complex sample environments, because of its large penetration, high angle resolution and low energy loss.27-29 To date, this technique is still rarely employed battery studies, most probably due to the less availability of related equipment.

Cylindrical 18650 Li ion battery (18 mm in diameter and 65 mm in length) is widely commercialized due to their high packing density and large safety. Many studies on the 18650 battery, documented in the literatures, focused on its electrochemical properties.30-31 Little work deals with the internal structure changes of 18650 battery, since the big diameter and stainless steel shell of the battery cause a large difficulty in the characterization by conventional techniques.

To reveal mechanistic and structural information during the lithiation/delithiation processes under non-equilibrium states, in situ HESXRD were employed to determine simultaneously the changes in both the cathode and anode in our previous paper,32-33 and this technique is proved to be effective for the study of battery. The only drawback in the previous work is that the time for every exposure is too long and only the average structure information during the exposure time is observed. In this paper, to observe more distinct structure information, the dynamic structure change of a commercial 18650 Li ion battery cycling under a high current density was investigated by using the time-resolved in situ HESXRD with an optimized exposure time.

**Experimental**

The high-resolution TEM (HRTEM) image the LiFePO$_4$ in the 18650 battery was obtained by JEOL 2100F (Japan) at 200 kV. A commercial 1.1 Ah 18650 cylindrical battery (Nanophosphat..
Results and Discussion

In order to check the thermal heat during the in situ HEXRD measurements we collect the 18650 battery temperature during cycling with and without in situ HEXRD measurements. Fig. 1 shows the surface temperature of the 18650 battery and reveals that the temperature did not increase when the battery is under high energy synchrotron XRD. For both temperature measurements, the heat was generated at the end of the charge/discharge process. The temperature fluctuation line is for the difference between the experimental and calculated data from the calculation with Rietveld refinement. Below the 1-D XRD pattern, the fitting of diffraction data is considerably reliable. It can be seen from Fig. 2 that various phases present in the battery, as marked below each diffraction peak in the 1-D XRD pattern, including cathode (LiFePO₄/FePO₄), anode (Li₄C₆), Al foil, Cu foil and stainless steel shell, can be identified in such a single XRD pattern in the 2θ range of 1°–4°. The Rwp factor is found to be as low as 2.14%, indicating a negligible heat effect of the high energy synchrotron XRD.

Fig. 2 shows the 2-D pattern of high energy synchrotron XRD for the 18650 battery at 0% state of charge (SOC) as well as the corresponding 1-D patterns before and after Rietveld refinement. Each diffraction ring in the 2-D pattern corresponds to a diffraction peak in the 1-D pattern, with the radius and integral area of diffraction ring corresponding to the 2θ angle and intensity of diffraction peak, respectively. The multiple-phase fitting of 1-D pattern has been performed via Rietveld refinement by using the GSAS software. After hundreds of fitting cycles, the Rwp factor is found to be as low as 2.14%, indicating that the fitting of diffraction data is considerably reliable. It can be seen from Fig. 2 that various phases present in the battery, as marked below each diffraction peak in the 1-D XRD pattern, including cathode (LiFePO₄/FePO₄), anode (Li₄C₆), Al foil, Cu foil and stainless steel shell, can be identified in such a single XRD pattern in the 2θ range of 1°–4° (d-spacing of 6.187 ± 1.547 Å). According to Bragg equation, the 2θ range of 1°–4° in the HESXRD (λ = 0.10798 Å) corresponds to that of 14.31°–59.70° in the conventional XRD (Cu Kα radiation source; λ = 1.54056 Å). Therefore, the information provided by the HESXRD can be enough to clarify the structure of electrode materials in the battery. One can also see from Fig. 1 that the diffraction peaks are well distinguished from each other, due to the large resolution of HESXRD, and the peak intensity is considerably large diffraction intensity in a short exposure time. The battery was placed horizontally with its axis being perpendicular to the X-ray beam (penetration depth ca. 12 mm). A MACCOR 4304 4 Channel Material and Cell Test System was used to charge/discharge the battery in the voltage range of 2.8–3.8 V at a constant current of 0.5 C, 4 C and 10 C. The surface temperature of the 18650 battery was recorded by the thermal couple on the surface of the battery. The successive collection of 2-D patterns with increasing charge/discharge time constructed the contour plots of diffraction patterns, after the 2-D patterns were converted into 1-dimensional (1-D) patterns. The 2-D patterns were calibrated by diffraction pattern of a standard CeO₂ sample and converted to 1-D patterns by using a Fit2D software. The lattice parameters of FePO₄/LiFePO₄ were obtained from the Rietveld refinement of 1-D pattern by GSAS suite of programs with the EXPGUI interface.

Figure 1. Comparison of the surface temperature of the 18650 battery without (a) and with (b) the in situ high energy synchrotron XRD. The battery is cycled between 2.8 V and 3.8 V at 4 C current rate.
high and contribution of amorphous phase (carbon black, electrolyte et al.) to the background is very little, because of the high flux of high energy X-ray beam and its low absorption by the illuminated materials. Apparently, the HESXRD pattern shows a good signal/noise ratio. The above result demonstrates that the HESXRD is fully competent in the in situ investigation of commercial batteries.

Fig. 3 shows the contour plots of HESXRD patterns (2θ = 0.8 ~ 2.8°) collected as a function of time during charge/discharge process as well as the corresponding voltage-time curve. The peak intensity is illustrated by the color scale at the right of figure. It should be mentioned that the diffraction peaks for Cu foil, Al foil and stainless steel shell all have an extremely high intensity and remain unchanged during the charge/discharge process, and thus, they are not included in the figure. One can see that all the contour plots of XRD patterns exhibit a good symmetry between the charge and discharge process, indicating that the charge and discharge processes are reversible and they follow the same mechanism. Due to this reason, only the structure changes during the charge process is discussed hereafter in this paper. Under the constant charge current of 4.4 A in our experiment, the capacity of the 18650 Li ion battery achieves ca. 1.045 Ah, being 95% of its theoretical capacity, at a 3.8 V cutoff voltage. It shows that the battery possesses an excellent cycle performance. As is known, during the battery charge, the deintercalation of lithium from LiFePO4 generates FePO4 and the intercalation of lithium into graphite leads to lithiated graphite. This process is well manifested by the changes in the HESXRD diffraction peaks. For the anode, the (002) reflection of graphite situates at 2θ = 1.833° before the charge of the battery, and it shifts toward lower 2θ angle during the charging process, generating the LiC6 phase. With increasing the charge time, the graphite (002) reflection shifts continuously toward low 2θ angle, passing through the cathode FePO4/LiFePO4 (111) reflection, until arrives finally at 2θ = 1.752° at 8.5 minutes, while its intensity decreases gradually. In addition, a new peak appears at 1.687°, along with the (002) reflection passing through the cathode (111) reflection, and its intensity increases with increasing the charge time. The new peak can be ascribed to the lithium-rich phase close to LiC6.28 For the cathode, the diffraction peaks of LiFePO4 (2θ = 1.201°, 1.583°, 2.229°, etc.) decrease gradually in intensity and disappear finally by the end of charge process, while the diffraction peaks of FePO4 (2θ = 1.253°, 1.647°, 2.283°, etc.) become strong. It can be concluded that the time-resolved changes in diffraction peaks, being an indicative of the structure changes in electrodes during cycling, have been effectively monitored by in situ HESXRD.

Fig. 4 shows the 1-D patterns of HESXRD during the charge process. All the patterns in the figure have been fitted through the Rietveld refinement method. The standard XRD patterns for FePO4, LiFePO4 and Li4C6 are also included as an inset in the figure. One can see that, with increasing the charge time, both the LiFePO4 (200) and (210) reflections decrease in intensity and their positions shift slightly toward high 2θ angle for charge time ≥ 10.5 minutes. At the very beginning of charge process, both the FePO4 (200) and (210) reflections have an abnormally high 2θ angle, particularly the later one that has overlapped with the week LiFePO4/FePO4 (011) reflections. With increasing the charge time, both the FePO4 (200) and (210) reflections increase in intensity and shift toward low 2θ angle till arrival at the normal position for charge time ≥ 5.1 minutes. The LiFePO4/FePO4 (101) reflection and (201)/(111) reflections for LiFePO4/FePO4 have degenerated respectively into a single peak, due to their very close 2θ angles. The onset of charge shifts the graphite (002) reflection toward low 2θ angle, transforming the graphite into a Li1.5C6 phase. With further increasing the charge time, the Li1.5C6 (002) reflection shifts continuously toward low 2θ angle and overlaps with the degenerate peak of LiFePO4/FePO4 (201)/(111) reflection until 7.4 minutes. The increase in the charge time to 8.5 minutes moves the Li1.5C6 (002) reflection out of the region of the degenerate peak of LiFePO4/FePO4 (201)/(111) reflection, and the further prolonging of charge time causes almost no change in 2θ angle but a gradual decreases in intensity of Li1.5C6 (002) reflection. In addition, from the charge time of 8.5 minutes, the diffraction peak at 2θ = 1.687°, corresponding to the new peak observed in Fig. 3, for the lithium-rich phase close to LiC6 also appears and its intensity increases obviously with increasing the charge time. One can also see that the baseline between the peaks for lithium-rich phase and Li1.5C6 rise (as the red circle marked in Fig. 3) with increasing the charge time, which may provide further prolonging of charge time causes almost no change in 2θ angle but a gradual decreases in intensity of Li1.5C6 (002) reflection. In addition, from the charge time of 8.5 minutes, the diffraction peak at 2θ = 1.687°, corresponding to the new peak observed in Fig. 3, for the lithium-rich phase close to LiC6 also appears and its intensity increases obviously with increasing the charge time. One can also see that the baseline between the peaks for lithium-rich phase and Li1.5C6 rise (as the red circle marked in Fig. 3) with increasing the charge time, which may provide another evidence to the finding, as reported in previous paper,38 that a series of intermediate phases between Li1.5C6 and LiC6 are formed. The above variations in the graphite anode can be interpreted as that the lithium intercalation into graphite under high current density follow a mechanism different from the classical stage mechanism, the details are reported in our previous paper.26

Fig. 5 shows the changes in both the cell volume and lattice parameters of LiFePO4/FePO4 during the charge/discharge process. All the data involved have been obtained basing on the Rietveld refinement. One can see that, for the LiFePO4 phase, with increasing the charge time, both the cell volume (291.2 Å3) and lattice parameters (a = 10.302 Å, b = 6.001 Å, c = 4.709 Å) remain almost unchanged till 10.5 minutes; the further prolonging of charge time leads to an obviously continuous decrease in both the cell volume and lattice parameter c and only a slight decrease in the lattice parameter a but a little increase in the lattice parameter b. At the 100% SOC (14.2 minutes),
Figure 5. Cell volume and lattice parameters \((a, b, c)\) for the LiFePO\(_4\) and FePO\(_4\) phases during the charge (left) and discharge (right) process. (Solid and hollow symbols are for the FePO\(_4\) and LiFePO\(_4\) phases, respectively. Lattice parameters: ■ and □, \(a\); ● and ◦, \(b\); ▲ and △, \(c\); ♦, cell volume).

The cell volume is 288.6 \(\text{Å}^3\) and parameters \(a\), \(b\), and \(c\) are 10.257 Å, 6.012 Å and 4.680 Å, respectively. For the FePO\(_4\) phase, the cell volume decreases from 282.0 \(\text{Å}^3\) to 274.0 \(\text{Å}^3\) and lattice parameters \(a\) and \(b\) from 10.095 Å to 9.871 Å and 5.918 Å to 5.822 Å, respectively, but the lattice parameter \(c\) increases from 4.720 Å to 4.769 Å, with increasing the charge time up till 5.1 minutes. The further increase in the charge time is found to cause almost very little change in both the cell volume and lattice parameters. The above results indicate that the whole charge process consists of three periods: Period I (charge time < 5.1 minutes), both cell volume and lattice parameters changes for FePO\(_4\) but not for LiFePO\(_4\); Period II (5.1 minutes ≤ charge time ≤ 10.5 minutes), both cell volume and lattice parameters do not change for FePO\(_4\)/LiFePO\(_4\); Period III (charge time > 10.5 minutes), the changes in both the cell volume and lattice parameters are just inverse to those in the period I. The variations in the FePO\(_4\)/LiFePO\(_4\) cathode during the discharge process is found to be just reverse to those during the charge process. It should be mentioned that the cell volume evolutions are different from our previous report. In the previous one, the cell volume for both LiFePO\(_4\) and FePO\(_4\) keeps decreasing during charge process while increasing during discharge process, and this trend remains consistent in different current rate. During a long exposure time, the internal structure changes were recorded in a single XRD pattern, and thus, the cell parameters are changing throughout the charge/discharge process. This will lead the observed results different from the actual mechanism. By shortening the exposure time, more distinct evolution of cell parameters are collected and the results obtained will more close to the real one.

Fig. 6 plots the peak intensities for (200) reflections of LiFePO\(_4\) and FePO\(_4\) during charge process. Since these two peaks are well-separated, their intensities, obtained by Rietveld analysis and Gaussian fits, are used to establish the phase fraction changes of LiFePO\(_4\) and FePO\(_4\). Interestingly, the changes of the peak intensities can be also divided into three similar periods as in the Fig. 5a (as shown by the dash line in Fig. 6). The peak intensities of LiFePO\(_4\) decrease lineally in period I and II while those of FePO\(_4\) increase lineally in period II and III (as shown by the solid line in Fig. 6). In period III and I, the changes of peak intensities for LiFePO\(_4\) and FePO\(_4\) deviate the linear trend respectively. All these phenomena suggest that the charge/discharge process may involve different lithium intercalation/deintercalation procedure in these three periods as it will be explained in the following paragraph.

There are predominantly two basic mechanisms in the literature to describe the procedures of lithiation/delithiation of FePO\(_4\)/LiFePO\(_4\), i.e., two-phase reaction\(^{17,39}\) and solid-solution reaction\(^{20,40–42}\) In the former mechanism, both the FePO\(_4\) and LiFePO\(_4\) are present as an individual phase, and according to the Gibbs phase rule, the reaction proceeds by varying the FePO\(_4\)/LiFePO\(_4\) ratio throughout the range of \(x\) in Li\(_x\)FePO\(_4\). The interface between the two phases shifts during the charge/discharge process, and accordingly, the cell volume and lattice parameters for both the FePO\(_4\) and LiFePO\(_4\) keeps constant. It was argued, however, that the formation and growth of second phase from either FePO\(_4\) or LiFePO\(_4\) have to overcome very large extra kinetic...
barriers, such as, nucleation of second phase, growth through interface, and coherency strain energy.43-44 In the second mechanism, only a single Li$_x$FePO$_4$ ($0 \leq x \leq 1$) phase is involved, and thus, both the cell volume and lattice parameters change continuously all through the lithiation/delithiation processes.20-21 This mechanism seems to be more favorable, since the solid-reaction is associated with a lower stress and mechanical degradation relative to the two-phase reaction, and it is theoretically predicted to occur under non-equilibrium conditions.23,45 However, the solid-solution reactions were only observed to occur for highly defective nanoparticles during heating the two-phase mixtures of FePO$_4$/LiFePO$_4$ with a range of particle-size distributions, and the stable phase of these systems at low temperatures was still a stoichiometric mixture of FePO$_4$ and LiFePO$_4$.26 Many researchers found that that lithiation/delithiation processes could occur via either two-phase or solid-solution reactions, dependent largely on the particle size, temperature, and current density.19 In addition, some reports revealed that the solid-solution and two-phase reactions could occur simultaneously.20,40,43 According to thermodynamics anticipation, there are two solid-solution regions outside the miscibility gap at a finite temperature in a binary system. The lithium-rich and lithium-poor end member phases were usually expressed as Li$_{1-x}$FePO$_4$ and Li$_x$FePO$_4$, notwithstanding the differences in the α and β values dependent on the morphology and dimension of LiFePO$_4$/FePO$_4$ particle size, charge/discharge rates and temperature. However, the intermediate phases within miscibility gap had been not yet clarified to be whether the fully lithiated (LiFePO$_4$) or delithiated (FePO$_4$) phases or the two separated phases with definite partial lithium occupancy and partial lithium defect in Li$_x$FePO$_4$.20,40,45 Apparently, the mechanism for the lithiation/delithiation processes still remain controversial.

In the present work, we find as pointed above that, in the period II, both the cell volume and lattice parameters for the LiFePO$_4$/FePO$_4$ phases do not change with charge time, indicating the presence of individual LiFePO$_4$ and FePO$_4$ phases. Both the cell volume and lattice parameters change for the FePO$_4$ phase but not for the LiFePO$_4$ phase in the period I, and they change for the LiFePO$_4$ phase but not for the FePO$_4$ phase in the period III. It indicates that the LiFePO$_4$ phase and a solid solution phase are present in the period I while the FePO$_4$ phase and another solid solution phase are present in the period III. The above phenomenon occurs most probably due that, in the period I, small amounts of lithium are released to generate some domains containing lithium vacancies in the LiFePO$_4$ matrix. Because of their low content and small dimension, the domains containing lithium vacancies can be partially relaxed to the LiFePO$_4$ matrix, leading to high concentration of lithium vacancies in the LiFePO$_4$ matrix. In another word, the loss of Li ions from local LiFePO$_4$ domains can be averaged among the LiFePO$_4$ domains, generating therefore the solid solution phase in the LiFePO$_4$ matrix, and due to the presence of lithium vacancies, both the cell volume and lattice parameters of lithium-deficient solid solution phase are different from those for either the LiFePO$_4$ or FePO$_4$ phases. Therefore, both the solid solution and individual LiFePO$_4$ phases are present concurrently in the period I. The reason that no FePO$_4$ phase is generated in the LiFePO$_4$ matrix is most probably due to the large extra kinetic barriers of such like nucleation, growth through interface motion and coherency strain energy.45 With the prolonging of charge time, more and more lithium are released, increasing both the dimension and concentration of lithium-deficient solid solution phase; meanwhile, the relaxation process mentioned above becomes difficult, due to the large diffusion barrier for lithium transfer from the LiFePO$_4$ matrix to the lithium-deficient solid solution phase, leading to high concentration of lithium vacancies in the latter phase. When lithium vacancies in the lithium-deficient solid solution phase contain a too much high concentration of lithium vacancies, they can be unstable and thus separate into the LiFePO$_4$ and FePO$_4$ phases, enabling the charge process enter the period II. In this period, the delithiation of LiFePO$_4$ phase with increasing the charge time generates directly the FePO$_4$ phase, without the formation of solid solution phase. This occurs due that the already-existing FePO$_4$ phase can catalyse the formation of the new FePO$_4$ phase, requiring no nucleation. With prolonging the charge time, the LiFePO$_4$ phase is continuously transformed into the FePO$_4$ phase, while its dimension decreases. When the dimension of LiFePO$_4$ phase has become so small to reduce largely the diffusion barrier, the lithium can be easily delocalized among the LiFePO$_4$ phase and surrounding FePO$_4$ domains. This leads to the generation of a lithium-rich solid solution phase in the FePO$_4$ matrix, and thus, shifts the charge process into the period III. In this period, the further prolonging of charge time decreases the dimension of solid solution phase, due to the delithiation, till a 100% SOC that transform the cathode completely into the FePO$_4$ phase. During the discharge process, the cathode undergoes a reverse process, relative to the charge process. The peak intensity changes of (200) reflections for LiFePO$_4$ and FePO$_4$ are also consistent with this proposed mechanism. When the two phase reaction mechanism occurs, the transition between LiFePO$_4$ and FePO$_4$ is in an equivalent amount, as a result, the peak intensities changes linearly. Once the solid solution phase emerges, the corresponding phase turns to a non-stoichiometric compound, leading to a non-linear change. Compared to our previous work,33 this mechanism shows the detailed collaboration between two phase reaction and solid solution mechanism at different period of charge/discharge process. In the middle of charge/discharge process (period II), the intercalation/deintercalation mechanism in this work is consistent with the traditional two phase reaction mechanism. However, at the beginning and ending of the charge/discharge process, instead of a dual-phase solid-solution reaction, only one solid solution phase is observed while the other one is the end member phase.

One may note that the above proposed mechanism for delithiation/lithiation is different from the mechanism of the concurrent occurrence of solid-solution and two-phase reactions reported in the literature, where two single solution phases are presented outside the miscibility gap. This occurs most probably due that the high current density has been applied in our work. Because of the dynamic delithiation process, the vacancies generated from the lithium release cannot be fast averaged all through the LiFePO$_4$ phase but only in local domains, generating therefore the solid solution phase in the LiFePO$_4$ matrix. The HRTEM image and particle size distribution of the nano LiFePO$_4$ in the 18650 battery are provided in Figure S1 in supporting information. It is found that nano LiFePO$_4$ particles are irregular in morphology with the mean size of $65 \pm 30$ nm. The size distribution of the LiFePO$_4$ particles is not very broad. It’s well known that the phase diagram strongly depends on the particle size because of the surface energy effect.45 Also, a completely solid solution phase is predicted in LiFePO$_4$ with particle size smaller than 15 nm at room temperature.40 During period I/II, the newly generated FePO$_4$/LiFePO$_4$ phases are pretty small, and thus the corresponding solid solution phases are presented. During period II/III, both FePO$_4$ and LiFePO$_4$ phases are bigger than the critical value for the solid solution phase, therefore, a two phase reaction is followed.

To confirm the proposed mechanism, the high energy synchrotron XRD are performed at current rate of 0.5 C and 10 C. The corresponding contour plots at different rate are shown in Figure S2 and S3 respectively. The contour plots are similar as the one at 4 C rate. Two independent phases are distinguished during the charge/discharge process, indicating a two phase reaction mechanism. To compare the difference, the changes of unit cell volume for LiFePO$_4$/FePO$_4$ during charge process are presented in Figure S4. The changes of unit cell volume also can be divided into three periods as in Fig. 3. However, the period I and III is much longer under 10 C than that under 0.5 C, and the presence of solid solution phase is much earlier in 10 C rate than that in 0.5 C rate while the disappearance of FePO$_4$ solid solution phase is much later in 10 C rate than that in 0.5 C rate. This phenomenon confirms our previous finding that the lithiation intercalation/deintercalation behavior is strongly dependent on the charge/discharge rate.43 Furthermore, it suggests that the solid solution mechanism trends to occur at high current rate while the two phase reaction mechanism prefers to occur at lower current rate.
Conclusions

The charge/discharge process in both the cathode and anode of a commercial 18650 lithium ion battery has been studied by in situ HESXRD technique under a current of 4.4 A (4 C). The results of the identification of phases and the changes on the graphite anode provide further evidences to the conclusion we reported previously that the intercalation/de-intercalation process under high current density follows a non-stage mechanism. With a shorter exposure time, a more distinct lithium intercalation/deintercalation mechanism in cathode is proposed in which the lithiation/delithiation of lithium comprises three periods, i.e., LiFePO$_4$ + lithium-deficient solid solution phases (period I), FePO$_4$ + LiFePO$_4$ phases (period II), and FePO$_4$ + lithium-rich solid solution phases (period III). The above mechanisms observed in the present work are different from those reported in the literature, and they can be ascribed to the lithium behaviors in the dynamic non-equilibrium state under high current density we applied, being contrastive to those in the thermodynamic equilibrium state. The in situ HESXRD technique, as shown in this work, is proved to be a very promising powerful tool for the studies on battery under real working condition.

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