Copper Phosphate as a Cathode Material for Rechargeable Li Batteries and Its Electrochemical Reaction Mechanism

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¶ Supporting Information

ABSTRACT: In the search for new cathode materials for rechargeable lithium batteries, conversion-type materials have great potential because of their ability to achieve high specific capacities via the full utilization of transition metal oxidation states. Here, we report for the first time that copper phosphate can be used as a novel high-capacity cathode for rechargeable Li batteries, capable of delivering a reversible capacity of 360 mAh/g with two discharge plateaus of 2.7 and 2.1 V at 400 mA/g. The underlying reaction involves the formation as well as the oxidation of metallic Cu. The solid-state NMR, in situ XAFS, HR-TEM, and XRD results clearly indicate that Cu can react with Li3PO4 to form copper phosphate and Li0.5CuPO4 during the charging process, largely determining the reversibility of Cu3(PO4)2. This new reaction scheme provides a new venue to explore polyanion-type compounds as high-capacity cathode materials with conversion reaction processes.

INTRODUCTION

Lithium ion batteries, a promising power system for hybrid and pure electric vehicles, have been widely used in various types of portable devices. Those important applications have driven the global search for novel electrode materials with higher specific capacities and energy densities.1−5 Certain promising anode materials, such as Si and Sn, have shown a large capacity of up to 3000 mAh/g.6−9 On the other hand, commercialized intercalation-type cathode materials exhibit much lower capacities, for example LiCoO2 (theoretical capacity: ∼ 274 mAh/g) and LiFePO4 (theoretical capacity: ∼ 170 mAh/g). Thus, cathode materials have become a technical “bottleneck” in the further development of Li-ion batteries with a high energy density.

Recently, many researchers have investigated several materials, such as Li,Mn9O4 and Cu2.33V4O11, which undergo multiple-electron reactions, leading to higher capacities for rechargeable Li batteries.10−16 However, the capacities of these materials have not yet been entirely realized. Poizot et al. found that Li3O can react with transition metals, M, in the charging process, thus enabling nanosized transition metal oxide (MO) particles (e.g., cobalt oxides) to exhibit high capacities by utilizing the full valence states of the metal.17 Unfortunately, among the M3N4 family of conversion materials (M = Fe, Co, Ni, Cu, etc.; N = N, O, F, P, S, etc.), only the MF6 family has...
shown sufficiently high conversion voltages to make them possible candidates for use as rechargeable Li battery cathodes.\textsuperscript{5,18−27} However, it is still important to explore new types of conversion-type cathode materials with different chemistries.

Many works have demonstrated that CuO can be used as an electrode material for lithium ion batteries, showing a relatively large capacity and good cycling performance.\textsuperscript{17,22} Replacement of oxide ions by phosphate may increase the conversion voltage, due to the inductive effect. Therefore, in this work, we revisit copper phosphate, a well-known cathode for primary batteries.\textsuperscript{59,60} To the best of our knowledge, this material has never been reported in the literature as a rechargeable cathode material. We observed for the first time that, by utilizing the Cu\textsuperscript{2+}/Cu\textsuperscript{0} redox reaction, a carbon-coated amorphous copper phosphate cathode was capable of delivering a reversible capacity larger than 360 mA/h/g at two discharge plateaus of 2.7 and 2.1 V with a high current density of 400 mA/g within 10 cycles. Additionally, both amorphous and crystalline materials were studied, showing that the material with an amorphous state delivered better electrochemical performance. This may be due to a more uniform distribution of reduction products.

Furthermore, we employed several techniques to understand the detailed reversible electrochemical reaction mechanism for this new type of rechargeable material. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM) were used to observe the morphology and fine structure of the material; high-resolution solid-state \textsuperscript{7}Li and \textsuperscript{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy was used to track the local structure and phase changes in the material;\textsuperscript{31−33} while X-ray absorption fine structure (XAFS) spectroscopy\textsuperscript{34,35} was implemented to investigate the oxidation state changes of Cu.

**RESULTS**

**Electrochemical Performance of the Cu\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}/C Cathode.** The rechargeability of transition metal phosphate as a conversion cathode material was demonstrated first. Figure 1a shows the discharge/charge profiles of the crystalline Cu\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}/C material operated between 1.5 and 4.8 V at a specific current of 10 mA/g. A capacity of up to 425 mA/h/g (theoretical capacity: 423 mA/h/g) was observed in the first cell had been discharged (or charged) to a certain state, charging was halted, and XAFS measurements were immediately performed. The XAFS data at the Cu K-edge were collected in transmission mode at room temperature, using ion chamber detectors at beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF) and a Si(111) double-crystal monochromator. The focal spot size at the position of the sample was 0.25 mm. The monochromator was calibrated to reject higher harmonics of the selected wavelength (harmonic content <10\textsuperscript{-4}), and data was collected over a range of energies, from 200 eV below to 800 eV above the Cu K-edge (8979 eV). The incident photon energy was calibrated using a standard Cu metal foil just prior to data collection in all in situ XAFS measurements. Processing and fitting of the XAFS data were performed using WinXAS software.\textsuperscript{67}

![Figure 1](image-url)
discharge, suggesting that the transfer of two electrons per Cu atom takes place and Cu$^{2+}$ is completely reduced to Cu$^0$ upon completion of the discharge. In the second cycle, the crystalline Cu$_3$(PO$_4$)$_2$ material displayed a reversible capacity of only 290 mAh/g (with 4.1 electrons per formula unit) in the second cycle and decayed quickly (Figure S1). Nevertheless, as shown in Figure 1b, the amorphous copper phosphate material exhibited much better cycling performance, with a reversible capacity larger than 360 mAh/g at 400 mA/g between 1.5 and 4.8 V (Figure 1b and Figure S1) within 10 cycles, meaning that 5.1 electrons per Cu$_3$(PO$_4$)$_2$ unit, or 1.7 electrons per Cu atom, are reversibly transferred. The capacity decayed to 220 mAh/g after 30 cycles, which may be due to the contact problem of reduction products and dissolution of Cu$_3$(PO$_4$)$_2$. The better cycling performance of the amorphous sample may be due to the smaller particle sizes of discharge products, copper and lithium phosphate in the amorphous sample, providing better physical contact between Cu and Li$_3$PO$_4$ thus facilitating the recharge reaction. Therefore, the cycling performance of the materials may be further improved through optimizing particle size and morphology. It should be noted that there were two clearer discharge plateaus, at 2.7 and 2.1 V, in the second discharge process, which may be due to the morphology changes. From the crystal structure of Cu$_3$(PO$_4$)$_2$ (Figure 2), it can be seen that there is no vacant site in the Cu$_3$(PO$_4$)$_2$ structure into which Li may insert, suggesting that a conversion reaction occurs even in the initial discharge process. Thus, the two discharge plateaus in the second discharge process may be due to different conversion reactions. As a new type of material for rechargeable Li batteries, the reaction mechanism may give us some important information. In order to understand the reactions of this new type of cathode, especially the two discharge plateaus and the recharging process, the crystalline material was examined in more detail, because of its high crystallinity and purity.

Crystal Phase Evolution Detected Using XRD. XRD is a very useful tool for monitoring crystalline phase changes during electrochemical reactions. Figure 3a depicts the XRD patterns of crystalline Cu$_3$(PO$_4$)$_2$ and Cu$_3$(PO$_4$)$_2$/C. A broader half peak width appeared in the XRD pattern of Cu$_3$(PO$_4$)$_2$/C, indicating that smaller particles were formed after ball milling, which brought about the rechargeable property. Figure 3b and Figure S2 are the XRD patterns of the material during the first two discharge/charge cycles. It can be clearly seen that the intensities of the XRD peaks corresponding to Cu$_3$(PO$_4$)$_2$ decreased, and a new and broad Bragg peak at 43.3° (attributed to Cu (111)) was detected when the x value in Li$_x$Cu$_3$(PO$_4$)$_2$ reached 2 during the first discharge, indicative of the decomposition of Cu$_3$(PO$_4$)$_2$ and the formation of metallic Cu during discharge. In the recharge process, the intensity of the 43.4° peak decreased, indicating that the copper was being reoxidized during the charge process. The discharge curve of the electrode (Figure 1) supports the claim of the complete conversion of Cu$_3$(PO$_4$)$_2$ to Li$_3$PO$_4$ and Cu metal when the discharge process is finished. However, no other new Bragg peaks were visible during cycling other than that at 43.3° (Cu(111)), indicating that Li$_3$PO$_4$ and any other products formed on recharging are amorphous and making it very difficult to obtain further structural information regarding any possible products and/or reaction intermediates from the powder XRD patterns. Nevertheless, the ex situ XRD study confirmed that Cu$_3$(PO$_4$)$_2$ was converted into copper during the discharge process, while the copper was reoxidized during the charge process.

Fine Structure and Differences between Amorphous and Crystalline Materials Observed with TEM. Figure 4 shows TEM images of both amorphous and crystalline materials at different stages (i.e., before discharge, after first discharge, and after first recharge). Figure 4a shows that the pristine amorphous (main image) material exhibits a large degree of disorder, and the crystalline (inset) Cu$_3$(PO$_4$)$_2$ sample possesses high crystallinity. Figure 4b demonstrates the submicron level structure of the discharged amorphous material. This structure consisted of often-interconnected particles, each several hundred nm in diameter and with a carbon coating of varied thickness (typically 5–20 nm). These larger particles were in turn formed from fairly uniform Cu nanoparticles, approximately 5 nm in diameter, and surrounding crystallites of Li$_3$PO$_4$ which can be seen in the image as dark “dots” and lighter regions, respectively. The discharged crystalline samples shared this general structure, but the constituent Cu nanoparticles exhibited a greater size as well.

Figure 2. Crystal structure of Cu$_3$(PO$_4$)$_2$ with the P-1 space group.

Figure 3. (a) XRD patterns of crystalline Cu$_3$(PO$_4$)$_2$ and Cu$_3$(PO$_4$)$_2$/C. (b) Ex situ XRD patterns of Li$_x$Cu$_3$(PO$_4$)$_2$/C.
as a wider size distribution, which are likely due to the larger contiguous Cu$_3$(PO$_4$)$_2$ regions in the pristine material. Figure 4c shows this structural model, in which the Li$_3$PO$_4$ and Cu regions are labeled in the amorphous sample that underwent a single discharge. The dark, circular areas correspond to Cu and the lighter surroundings, Li$_3$PO$_4$. The Li$_3$PO$_4$ was in the form of small crystallites for both amorphous and crystalline samples, although it was difficult to determine if the average Li$_3$PO$_4$ crystallite size differed between these two. Finally, Figure 4d shows the crystalline sample after the first recharge. Areas of Cu and Cu$_3$(PO$_4$)$_2$ are seen, demonstrating the incomplete reaction of Cu with surrounding Li$_3$PO$_4$ and the presence of substantially larger Cu nanoparticles compared to amorphous samples, which is in accordance with the XAFS results (Figure 8a). However, the TEM imagery of amorphous samples after the first recharge did not display any crystal planes of Cu$_3$(PO$_4$)$_2$, indicating that the recharged material was highly amorphous. This TEM data is consistent with the previous observation: the degree of disorder of Cu$_3$(PO$_4$)$_2$ crystals in the pristine material had an impact on the charge capacity of the sample. The material with higher crystallinity formed larger Cu nanoparticles upon discharge and larger regions of Cu$_3$(PO$_4$)$_2$ upon recharge, presumably interfering with Li ion transport during the reaction process and leaving “islands” of unreacted material dispersed throughout the structure.

Local Structure Changes during Cycling Detected by Solid-State NMR. High-resolution solid-state NMR is a powerful method for understanding the local structure of materials, especially those in amorphous states. Figure 5 shows the mass-normalized $^7$Li MAS NMR spectra of crystalline Cu$_3$(PO$_4$)$_2$/C during the first discharge and second charge processes. The inset is the enlarged view of selected states. Upon discharge, two peaks at −0.3 and −13 ppm were observed, as shown in Figure 5a ($x = 0.3, 2.7$ V). The peak at −13 ppm can be assigned to the Li close to Cu$^{2+}$ (3d$^9$), as the unpaired electrons from paramagnetic Cu$^{2+}$ causes a large shift due to Fermi-contact interactions. The peak at −0.3 ppm was due to the Li located in a diamagnetic environment. In addition, it can be clearly seen that the line-width of the −0.3 ppm peak has a trend of being reduced during discharge. Since the material was completely converted to Cu metal and Li$_3$PO$_4$, the peak at −0.3 ppm in Figure 5a ($x = 6.0$) could be confidently assigned to Li$_3$PO$_4$. The −0.3 ppm peak with a relatively broader line-width for other discharge states ($x = 0.3, 1.0, 2.0$) may indicate the formation of another diamagnetic environment during the discharge process, such as Cu$^{+}$ (3d$^{10}$), with strong evidence for this provided by XAFS results (Figure 8a).

Figure 5b presents the $^7$Li NMR spectra during the charge process in the second cycle. The decrease in the intensity of the −0.3 ppm peak indicated that the Li in Li$_3$PO$_4$ deintercalated during the charge process. As shown in the inset of Figure 5b,
when the material was charged to 2.7 V only one peak at −0.3 ppm with decreased intensity and a slightly broader line-width was observed compared to the discharged sample, which may be due to the formation of Cu'. Another peak at −13 ppm could be seen when the voltage reached 3.3 V. As mentioned before, the $^7$Li NMR peak at −13 ppm was due to the Li located around the Cu$^{2+}$. Thus, we can conclude that Cu was oxidized to Cu' when the voltage was below 2.7 V, while Cu$^{2+}$ was formed afterward. However, the intensity of the peak at −13 ppm did not increase in the following charge process, indicating that another compound without Li formed. The discharge in the second cycle shows reaction processes similar to the first cycle, as shown in Figure S3. The intensity of the peak at −13 ppm increased when the material discharged to 2.7 V and decreased when the voltage was 2.0 V, indicating that Cu$^{2+}$ and Li$^+$ contained intermediates that primarily formed when the discharge voltage was larger than 2.7 V and converted into Li$_2$PO$_4$ when the discharge voltage was lower than 2.5 V.

Figure 6 shows the mass-normalized $^{31}$P NMR spectra of crystalline materials at different discharge states, giving more detailed information regarding the reaction products. The $^{31}$P peaks between 1500 and 2000 ppm were assigned to crystalline Cu$_3$(PO$_4$)$_2$. The $^{31}$P resonance of paramagnetic Cu$_3$(PO$_4$)$_2$ will shift under different temperatures, and although the room temperatures when testing different samples were the same, the real temperatures of the samples in the high-spinning rotors may have been different, due to the unavoidable presence of Al pieces scraped from the electrodes. Differing amounts of Al cause different temperature rises under a spinning frequency of 60 kHz, resulting in different chemical shifts observed for Cu$_3$(PO$_4$)$_2$. However, the same $^{31}$P shifts were obtained under a low spinning frequency of 25 kHz, as shown in Figure S4. Figure 6a depicts the $^{31}$P NMR spectra of the crystalline material when the x value in Li$_x$Cu$_3$(PO$_4$)$_2$ was less than 2. In addition to the peak assignable to crystalline Cu$_3$(PO$_4$)$_2$, a peak at around 9 ppm, whose line-width at half height decreased with discharge, can be assigned to Li$_2$PO$_4$ and diamagnetic species, which was in accordance with the $^7$Li NMR results. Therefore, we can conclude that the diamagnetic intermediate formed in the discharge process was Li$_x$Cu(II)PO$_4$. The reduction in the line-width may have been due to the decomposition of Li$_x$Cu(II)PO$_4$ and the formation of Li$_y$PO$_4$. Additionally, a broad $^{31}$P peak at around 400 ppm was observed, which was due to the P close to Cu$^{2+}$. The intensity of the broad peak at around 400 ppm increased with discharge when the x value was less than 2 and then decreased in the following discharge process. When the x value reached 5, the peak almost vanished, as shown in Figure 6b. Figure 7a shows the $^{31}$P NMR spectra of the material during the charge process in the second cycle. It can be seen that the broad peak at around 400 ppm was obtained again when the charge voltage reached 3.3 V. Considering that almost the same trend of the $^7$Li peak at −13 ppm and the broad $^{31}$P peak at around 400 ppm can be found during the first and second cycles, it is reasonable to believe that the Li−Cu(II)−P−O compound formed during the discharge/charge processes. The general material formula Li$_x$Cu(II)PO$_4$ will be used here. This Li$_x$Cu(II)PO$_4$ formed mainly when the charging voltage was lower than 3.3 V. However, another compound formed in the following charge process. As shown in Figure 7a, a very
Figure 8. (a) The first derivative curves of in situ XANES spectra (black) and the linear combination fitting curves (red), obtained using the first derivative XANES curves of Cu$_3$(PO$_4$)$_2$ (x = 0) and Li$_x$Cu$_3$(PO$_4$)$_2$ as standards. The vertical axis (x) indicates the corresponding value in Li$_x$Cu$_3$(PO$_4$)$_2$. (b) Discharge/charge profiles and fitting results (coordination numbers and bond lengths) for Cu–O and Cu–Cu from the in situ EXAFS data.

broad $^{31}$P peak between 500 and 3000 ppm was observed when the material was charged to 4.0 V. The ex situ $^7$Li NMR spectra during the charge process demonstrates that a compound without Li was possibly formed when the material was charged to 4.0 V. Additionally, the $^{31}$P shift of amorphous copper phosphate was observed to be between −500 and 4000 ppm (Figure S5). Therefore, the broad peak between 500 and 3000 ppm can be assigned to the amorphous copper phosphate. In other words, amorphous copper phosphate formed when the charge voltage reached 4.0 V. Figure 7b is the $^{31}$P NMR spectra of carbon coated crystalline materials during the second discharge process. It can be seen clearly that the intensity of the signal from the amorphous copper phosphate decreased with discharge, and the peak from Li$_x$Cu$_3$(II)PO$_4$ was reduced when the voltage was up to 2.0 V, which was consistent with the $^7$Li NMR results. It should be noted that a recycle delay of 0.01 s was applied for the acquisition of $^{31}$P NMR spectra, allowing a full relaxation when using a recycle delay of 0.01 s. However, the relaxation times of the $^{31}$P peaks corresponding to copper phosphate and Li$_x$Cu$_3$(II)PO$_4$ were much less than 1 ms, allowing a full relaxation when using a recycle delay of 0.01 s. The $^{31}$P NMR spectra at different states using a recycle delay of 60 s are shown in Figure S6.

The high-resolution solid-state $^7$Li, $^{31}$P MAS NMR spectra thus demonstrate that two intermediate compounds, Li$_x$Cu(I)PO$_4$ and Li$_x$Cu(II)PO$_4$, were formed during the first discharge process. When $x$ was larger than 2, the conversion reaction of Cu$_3$(PO$_4$)$_2$ and Li$_x$Cu(I, II)PO$_4$ into Li$_x$PO$_4$ was mainly occurring. The charge process of the material underwent three reaction processes. First, Li$_x$Cu(I)PO$_4$ formed, while the voltage was less than 2.7 V. Second, when the voltage was between 2.7 and 3.3 V, the formation of Li$_x$Cu(II)PO$_4$ dominated. Finally, when the voltage was above 3.3 V, amorphous copper phosphate was the primary reaction product. In addition, the second discharge process looks like the reverse of the charge process. Li$_x$Cu(I)PO$_4$ and Li$_x$Cu(II)PO$_4$ were formed when the discharge voltage was larger than 2.7 V, and Li$_x$Cu(II)PO$_4$ started to convert into Li$_x$PO$_4$ when the voltage was lower than 2.5 V.

**Tracking Cu Oxidation States and Local Structure Changes Using in Situ XAFS.** The XAFS study gives a direct view of the oxidation of copper. Figure 8a shows first-derivative curves of in situ X-ray absorption near-edge structure (XANES) spectra (black) and linear combination fitting curves (red), obtained using the first-derivative XANES curves of the crystalline Cu$_3$(PO$_4$)$_2$ electrode and fully discharged Li$_x$Cu$_3$(II)PO$_4$ as standards. It can be clearly seen that in addition to the peaks located at 8979 eV (Cu) and 8984 eV (Cu$^{2+}$), a signal was also observed at 8981.4 eV in the discharge/charge spectra, which can be attributed to the Cu$^{+}$ ion. Due to the fact that the valence state of copper in Cu$_3$(PO$_4$)$_2$ is Cu$^{2+}$, we can deduce that the Cu$^{+}$ is present in the intermediate product, Li$_x$Cu(I)PO$_4$. These results agree well with evidence from NMR testing. The first-derivative spectra and XANES spectra (Figure S7) reveal that the formation of Cu$^{+}$ in the first discharge process occurred mainly before the $x$ value in Li$_x$Cu$_3$(PO$_4$)$_2$ reached 0.5 and decreased slowly until disappearing when $x$ increased to 5.5. Combining these results with the observation of the continuously increasing intensity of the $^7$Li peak at $−0.3$ ppm (Figure 5a) and $^{31}$P peak at 9 ppm (Figure 6a), we can tell that Li$_x$PO$_4$ formed continuously during discharge and was the main discharge product during the whole discharge process. During charging, the amount of Cu$^{+}$ was found to gradually increase as $x$ decreased, demonstrating the continuous formation of a small amount of Li$_x$Cu(II)PO$_4$ during the charge process. Of course,
the main reaction was the oxidation of Cu to Cu$^{2+}$, which is shown clearly in Figures S7 and S8. Additionally, the peak at 8979 eV was observed in the XANES spectrum of Li$_3$Cu$_2$(PO$_4$)$_2$, indicating that Cu metal formed as soon as the battery began discharging; thus, a complex reaction mechanism involving Cu metal formation could be anticipated. Additionally, the XAFS data shows that the local environment of Cu changes during the discharge/charge process. Figure 8b shows the bond lengths of Cu–O and Cu–Cu, as well as their coordination number (CN), during cycling. Both Cu–O and Cu–Cu bond lengths remained relatively unchanged throughout this process; however, the CN of Cu–O decreased with discharging, while that of Cu–Cu increased. On charging, these trends were reversed. The increasing CN of Cu–O demonstrated that Cu was oxidized to a Cu$^{2+}$ containing compound, in accordance with the NMR results. Furthermore, the decreasing CN of the Cu–Cu unit indicated that the particle size of Cu decreased with charging, which was due to the reaction of Li$_3$PO$_4$ and Cu to form Li$_3$Cu$_2$(PO$_4$). Of note is the fact that the Cu–Cu CN for the discharged material was about 9, which was less than that of bulk Cu (12), indicating that Cu metal nanoparticles were formed. Furthermore, some Cu–Cu bonding was retained even after the battery was fully charged, indicating that some unreacted Cu was still present even at 4 V, which is consistent with the TEM results.

The XAFS study confirmed the existence and change of Cu$^+$ in the intermediates Li$_3$Cu$_2$(PO$_4$) during the cycling of crystalline copper phosphate. Additionally, it revealed that a Cu mass was formed upon discharge, and then was reoxidized to Cu$^+$ and Cu$^{2+}$ during the charging process. The analysis results from XAFS are highly consistent with those from NMR.

**CONCLUSION**

The Cu$_3$(PO$_4$)$_2$ material has superior characteristics that make it suitable, with some additional process tuning, as a cathode material for lithium ion batteries. Due to the inductive effect of the phosphate group, the Cu$_3$(PO$_4$)$_2$ shows a higher working voltage of 2.7 and 2.1 V compared to CuO (1.5 V). Furthermore, it is possible to control/select the discharge voltage by changing the transition metal and anion group materials. Presently, the material can deliver a reversible high capacity of larger than 300 mAh/g within 20 cycles at high current density. The reversibility of the material is very sensitive to the particle size; the as-prepared crystalline sample shows almost no cycle performance. However, the ball-milled carbon coated sample, which has smaller particles, displays reversibility. In addition, the amorphous material has a better rechargeability. Considering the different morphologies of the discharged crystalline and amorphous samples as given by TEM results, we can deduce that the rechargeability of Cu$_3$(PO$_4$)$_2$ depends strongly on the particle sizes of the discharge products but not that of the pristine samples (Figures S10 and S11). It is speculated that the smaller particle size of the Cu and Li$_3$PO$_4$ phases formed during discharge leads to a more uniform reaction product distribution and provides better contact between Cu and Li$_3$PO$_4$, thus facilitating the recharge reaction (oxidation of Cu). In addition, the high diffusivity of copper ions in the polyanion framework could be another factor that affects the reversibility of the conversion reaction in Cu$_3$(PO$_4$)$_2$. Although the capacity of the material currently decays to 220 mAh/g within 30 cycles, it is likely to be improved after introducing morphology and size control.

Several local structure characterization techniques such as XAFS, NMR, and XRD have been carried out to probe the crystal and local structure changes in the nanostructured Cu$_3$(PO$_4$)$_2$ during the discharge/charge processes and thus to understand these complex conversion reactions, as summarized in Figure 9. In the first discharge process, small amounts of Li$_x$Cu(II)$_x$PO$_4$ were formed when the x value in Li$_x$Cu$^{(II)}$(PO$_4$)$_2$ was less than 0.5, material that was gradually reduced to Cu and Li$_3$PO$_4$ in the following discharge process. The result was strongly supported by in situ XAFS study. However, this is only a side reaction. Li$_3$PO$_4$, Li$_3$Cu(II)$_x$PO$_4$, and Cu are the three main products when the x value in Li$_x$Cu$^{(II)}$(PO$_4$)$_2$ is less than 2. Moreover, the reduction of both Cu$_3$(PO$_4$)$_2$ and Li$_3$Cu(II)$_x$PO$_4$ to Li$_3$PO$_4$ and Cu primarily occurred during subsequent discharge processes. In the charge process, Li$_3$PO$_4$ and Cu were converted to Li$_x$Cu(II)$_x$PO$_4$ when the voltage was less than 2.7 V. Subsequently, Li$_x$Cu(II)$_x$PO$_4$ was primarily formed until the voltage reached 3.3 V, where amorphous copper phosphate started to generate. The second discharge curve showed two clear plateaus at 2.7 and 2.1 V. However, the reactions in the
second discharge process were similar to the first discharge. Amorphous copper phosphate converted to Li,Cu(II)PO₄, Li₃PO₄ and Cu before 2.7 V, and then Li,Cu(II)PO₄ and amorphous copper phosphate were reduced to Cu and Li₃PO₄. The discharge plateau at 2.7 V in the second cycle had larger capacity than that in the first cycle, which may be due to morphology change after the first discharge. A surface with higher specific area may form, facilitating the reaction. It is well-known that the transition metal oxides, MO, can be used as conversion electrodes for lithium ion batteries. However, the low conversion voltages of MO have thus far been insufficient for use as cathode materials. By contrast, polyaniion compounds display a higher conversion voltage because of the stronger inductive effect of the polyanion groups. Our results indicate that transition metals, M, such as Cu, and Li₃PO₄ can be converted into Li,MPO₄, which holds important implications for the further optimization of these materials and the design of new polyaniion-type cathode materials with large specific capacities.

■ ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b02290.

Detailed information for the whole set of XRD patterns, NMR spectra, TEM figures, XANE spectra, and fitting curves of extended k-weighted EXAFS spectra during cycling of the material (PDF).

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Author Contributions
G.Z. and J.B. contributed equally. G.Z., J.B., and Q.L. carried out the materials preparation and electrochemical test. G.Z. and X.H. acquired the material data, G.Z., R.F., and J.A.T. analyzed the NMR data. G.Z., W.Y., and Z.G. carried out the XAFS experiments. G.Z., P.N.D, and P.Z. processed and analyzed the XAFS data. M.M. and W.Z. recorded and analyzed the TEM results. Q.L. acquired and processed the XRD data. Y.Y. and G.Z. proposed the research, and Y.Y. attained the main financial support for the research.

Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Whittingham, M. S. Lithium batteries and cathode materials. 


(7) Chen, H.; Xiao, Y.; Wang, L.; Yang, Y. Silicon nanowires coated with copper layer as anode materials for lithium-ion batteries. J. Power Sources 2011, 196, 6657–6662.


(16) Gong, Z.; Yang, Y. Recent advances in the research of polyanion-type cathode materials for Li-ion batteries. Energy Environ. Sci. 2011, 4, 3223–3242.


