What Happens to LiMnPO₄ upon Chemical Delithiation?

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Supporting Information

ABSTRACT: Olivine MnPO₄ is the delithiated phase of the lithium-ion-battery cathode (positive electrode) material LiMnPO₄, which is formed at the end of charge. This phase is metastable under ambient conditions and can only be produced by delithiation of LiMnPO₄. We have revealed the manganese dissolution phenomenon during chemical delithiation of LiMnPO₄ which causes amorphization of olivine MnPO₄. The properties of crystalline MnPO₄ obtained from carbon-coated LiMnPO₄ and of the amorphous product resulting from delithiation of pure LiMnPO₄ were studied and compared. The phosphorus-rich amorphous phases in the latter are considered to be MnH₂P₂O₇ and MnHP₂O₇ from NMR, X-ray absorption spectroscopy, and X-ray photoelectron spectroscopy analysis. The thermal stability of MnPO₄ is significantly higher under high vacuum than at ambient condition, which is shown to be related to surface water removal.

INTRODUCTION

Olivine-type LiMPO₄ (M = Fe, Mn, Co, and Ni) is a promising class of cathode materials for lithium-ion batteries. LiFePO₄ is used as a power source for electric vehicles owing to its safety, long-term cycle life, and significantly improved power density. LiMnPO₄ could be a good substitute for commonly used long-term cycle life, and significantly improved power density. LiFePO₄ is used as a power source for electric vehicles owing to its safety, long-term cycle life, and significantly improved power density. LiMnPO₄ could be a good substitute for commonly used cathode materials because it has higher voltage (4.1 V vs Li⁺/Li) and higher energy density.6–9 However, LiMnPO₄ has low electronic conductivity,7 local structure distortion caused by Jahn–Teller active Mn²⁺ ions,8–10 and a large cell volume change between LiMnPO₄ and MnPO₄ during the charge/discharge process,11 along with a metastable delithiated phase.12

Safety is one of the most important criteria for commercialization of cathode materials, and the delithiated phases MPO₄ are relatively unstable compared to their lithiated forms, especially for Mn and Co.16,17 These phases have not been synthesized directly so far, and chemical delithiation is the only method that allows investigation of the intrinsic thermal property of the materials without the influence of conductive agents and binders.18 However, the chemical delithiation process corresponds to a potentiostatic (constant-voltage) charging, and the redox potentials of most commonly used oxidizing agents are higher than needed to oxidize LiMPO₄. Thus, sometimes the driving force for chemical delithiation is high enough to damage the MPO₄ structure.19 Also, the mechanism of Li⁺ and e⁻ transformation through chemical delithiation may be different from electrochemical delithiation, which is usually done at small constant current.20,21

We earlier reported the structural and thermal stability of crystalline MnPO₄ under ambient conditions and revealed the critical role of carbon coating.22 We found an amorphous phase forming after chemical delithiation for LiMnPO₄ with no carbon. Such amorphization during chemical delithiation has also been reported by Yamada et al.,5 Masquelier et al.,7 and Park et al.23 We also observed a significant water content, including surface water and crystalline water, in the delithiated products by thermogravimetric analysis (TGA)–mass spectrometry (MS). The crystalline MnPO₄ has ~5% water, while the amorphous product has more than 15% water.

Here, the goal is to determine the inherent stability of olivine MnPO₄ and to understand how amorphization occurs upon chemical delithiation. Thus, we focus on the composition of the amorphous delithiated LiₓMnPO₄ as well as on the stability of crystalline MnPO₄ under high vacuum, where the surface water is removed. Because of the amorphous nature of the delithiation products, along with X-ray diffraction (XRD) and TGA–MS, we apply a variety of surface and local characterization techniques, including X-ray photoelectron spectroscopy (XPS), in situ X-ray absorption spectroscopy (XAS), in situ transmission electron microscopy (TEM), and NMR, to

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investigate the atomic and electronic structure of amorphous MnPO₄ and its stability.

## EXPERIMENT

LiMnPO₄ was synthesized by a solid-state method at 600 °C with intermediate heating at 350 °C in a helium atmosphere from Li₂CO₃ (Fisher, ≥99%), MnAc, 4H₂O (Aldrich, ≥99%), and NH₄H₂PO₄ (Aldrich, 99.99%) precursors. The details of the synthesis can be found elsewhere.²² LiMnPO₄ so obtained is referred to as LMP-RC, where RC indicates residual carbon from carbonate and acetate precursors. The LMP-NC (no carbon) was synthesized by the same method, except that the final annealing was performed in an oxygen atmosphere at 600 °C.

MnPO₄ was obtained by chemical delithiation using NO₂BF₄ as the oxidizing reagent. A total of 800 mg of LiMnPO₄ was dispersed in 50 mL of acetonitrile, and then 3-fold excess NO₂BF₄ was added to the solution in a nitrogen-filled glovebox. The solution was stirred for 6 days, then filtered and washed with acetonitrile, ethanol, and acetone, and finally dried overnight.²² The MnPO₄ samples are named following the names of their parent compounds by replacing LMP with MP.

The phase purity and crystal structure were characterized using powder XRD, where data were collected on a Scintag XDS2000 powder diffractometer equipped with a Ge(Li) solid-state detector and a Cu Kα sealed tube (λ = 1.54 Å). Rietveld refinement of the XRD patterns was performed using the GSAS/EXPGUI package.²⁴ In situ high-temperature XAS at Mn K-edge (6539 eV) was performed at the Advanced Photon Source, Beamline SBM. MP-NC powder was diluted by boron nitride and pressed into a pellet of ~1 cm diameter, which was loaded in a Linkam THMS600 heating stage for the heating experiment under the protection of an inert gas (nitrogen). Different heating rates were applied to the two regions: 5 °C/min over the temperature ranges of 25–100 and 200–300 °C and 2 °C/min over 100–200 °C. XAS data were collected at every 10 °C as the desired temperature was stabilized. XAS data were processed and analyzed using the IFEFFIT package.²⁵ The thermal properties of the samples were examined by TGA (PerkinElmer TGA 7). In a nitrogen atmosphere, the sample was heated to 100 °C at 5 °C/min and held for 16 h. Then the sample was continually heated to 600 °C at 5 °C/min, held for 1 h, and finally cooled to room temperature. The stoichiometries of Li, Mn, and P were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Axial MPX).

XPS of MnPO₄ powders was performed using a Phi VersaProbe 5000 system with a monochromated Al Kα source and a hemispherical analyzer. The powders were pressed into pellets before the measurements to avoid the use of adhesive tape during the heating process. The core levels (Mn 2p, P 2p, O 1s, and C 1s) and the valence-band region were measured with a pass energy of 23.5 eV, corresponding to an instrumental resolution of 0.51 eV from analysis of both the Au 4f½ and Fermi edge of the gold foil. The binding-energy scale was calibrated to the C 1s core-level peak to account for sample charging effects. Following the initial XPS measurements, the samples were transferred to a heating stage in vacuo, heated from room temperature to 700 °C at a rate of 5 °C/min, and held at 700 °C for 30 min. The residual gases during the heating process were monitored using an SRS RGA200 mass spectrometer. Postheating XPS was then measured after the samples returned to room temperature. Finally, the samples were removed from the XPS chamber, and their XRD patterns were taken.

TEM samples were prepared by the powder sample preparation method with ultrasonic dispersion followed by drop casting onto a lacey carbon film supported by a TEM molybdenum grid purchased from Ted Pella, which was then mounted onto a Gatan heating holder with rapid heating capability using a Gatan hot-stage temperature controller. Structure and phase evolution were investigated by selected-area electron diffraction (SAED) on a JEOL JEM2100F transmission electron microscope operated at 200 kV. In order to minimize the beam effect, the electron dose was reduced during imaging. The diffraction patterns from different areas were taken during in situ heating to avoid the beam effect. The heating rates of MP-RC and MP-NC were 3 and 5 °C/min, respectively. For ex situ heating experiments, samples were heated from room temperature to 600 °C at a rate of 5 °C/min in air and held for 1 h. After cooling, SAED patterns of the products were taken to compare with the results of the in situ TEM heating experiments.

Solid-state NMR experiments²⁶ were performed on a Bruker Avance III 200 spectrometer using a Bruker 1.9 mm magic-angle-spinning (MAS) probe with MAS frequencies varying in the range 35–40 kHz. 1H NMR spectra were acquired using a rotor-synchronized Hahn echo sequence with a radio-frequency (RF) pulse amplitude equal to 125 kHz. Resonances were referenced to adamantane set at 1.8 ppm.³¹P NMR spectra were acquired with a rotor-synchronized Hahn echo sequence as well as the projected–magic angle turning phase adjusted sideband separation (projection MATPASS) two-dimensional experiment for spinning sideband separation. For both experiments, a RF amplitude of 147 kHz was used and resonances were referenced to ammonium dihydrogen phosphate set at 0.8 ppm. Hahn echo spectra for MP-NC were acquired by summing four experiments with variable offsets (centered at 4500, 6000, 7500, and 9000 ppm) and 11 experiments for MnHPO₄ (offset varying from 0 to 10000 ppm in steps of 1000 ppm). Relaxation delays were optimized for each sample and nucleus and varied between 2 and 6 s for 1H and between 10 and 50 ms for ³¹P.

## RESULTS AND DISCUSSION

The XRD patterns of the LiMnPO₄ samples (Figure S1) show a single phase with orthorhombic structure and unit cell parameters [a = 10.449(1) Å, b = 6.105(1) Å, and c = 4.746(1) Å] that are similar for LiMnPO₄ both with residual carbon and with no carbon (Table S1). The cell volumes are close to the literature value of 303.2 Å³.²⁸ The XRD patterns (Figure 1) of chemically delithiated samples reveal the olivine MnPO₄ phase in MP-RC, with a small amount of the Mn₃P₂O₇ phase present in some samples. Rietveld refinement (Table S1) shows that the unit cell parameter of MP-RC is similar to that of our previous work.²² According to our previous study,²² the residual carbon content is ~0.3 wt %. In contrast, MP-NC is basically amorphous with some weak and broad peaks of MnPO₄ recognizable in the XRD pattern. Such amorphous nature of MP-NC is also confirmed by TEM (Figure 2).

The composition of the delithiation products determined by ICP-OES (Table 1) shows that there is no lithium in either MP-RC or MP-NC; however, manganese deficiency is observed in both samples. Such manganese deficiency may indicate the existence of a second phosphorus-rich amorphous phase.

One of the most possible reasons for manganese deficiency is manganese dissolution into the solvent during chemical delithiation. ICP-OES was used to analyze the element concentration in the solutions that remained after this process. We collected the original solvent solution (called original). Then we used acetonitrile, ethanol, and acetone to wash the samples and collected this portion of the solution (called wash) as well. According to the ICP results (Table 2), the element concentration in the wash solution is 1 order of magnitude less than that in the original solution, so dissolution occurs upon chemical delithiation, while the influence of the subsequent wash is negligible. It is also interesting to note that, in the case of MP-RC, manganese and phosphorus are being dissolved in a ratio of 1.34:1, while from MP-NC, more than three manganese atoms per phosphorus are dissolved. This is consistent with the higher manganese deficiency found in the MP-NC sample. Furthermore, we observe that the crystallinity of MnPO₄ diminishes as the manganese deficiency increases.
To further understand the nature of the delithiated products, we used an XPS technique to investigate their surface composition, manganese oxidation states, and electronic structures. Figure 3 shows the Mn 2p, C 1s, and valence-band XPS spectra collected from the MP-RC and MP-NC samples. The C 1s spectra show the typical surface carbon species centered around 285 eV in both samples, as well as a small peak at higher binding energy representative of the residual carbon only seen in the MP-RC spectra. In the Mn 2p core-level spectra, the main Mn 2p3/2 peak is at 642 eV, representing Mn3+, while an additional shoulder at lower binding energy is observed for MP-NC. This indicates that manganese has mixed valences of 2+ and 3+ in MP-NC, while MP-RC shows mainly Mn3+. This is in agreement with the XAS results to be discussed in detail later. From analysis of the core-level XPS, the atomic composition at the surface shows manganese deficiency and no lithium in both MP-RC and MP-NC, which is in good agreement with the ICP-OES results. The valence band of MP-RC most closely resembles that of the pure crystalline phase MnPO₄, although the features are less pronounced, as is expected. In the valence-band spectra of MP-NC, there is a feature at ~15 eV, which is less pronounced in MP-RC. This is a key signature of the pyrophosphate phase. This is evidence that some pyrophosphate species may exist in the amorphous phase.

According to the TGA–MS experiments in our previous study, upon heating, MP-RC and MP-NC show abnormal weight loss (about 10 and 20 wt %, respectively), with two peaks related to water loss occurring at 100 and 300 °C. Thus, here we aim to investigate the nature of water (or protons) in the samples and to understand their influence on the composition, manganese oxidation states, and electronic structures. Figure 3 shows the Mn 2p, C 1s, and valence-band XPS of MP-RC and MP-NC.

Table 1. ICP Results of MP-RC and MP-NC

<table>
<thead>
<tr>
<th></th>
<th>Li/Mn/P ratio</th>
</tr>
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<tr>
<td>MP-RC</td>
<td>0.00:0.84:1.00</td>
</tr>
<tr>
<td>MP-NC</td>
<td>0.00:0.65:1.00</td>
</tr>
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Table 2. ICP Results of Chemical Delithiation and Washing Solutions

<table>
<thead>
<tr>
<th></th>
<th>manganese (ppm)</th>
<th>phosphorus (ppm)</th>
<th>Mn/P molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP-RC original</td>
<td>39.59</td>
<td>16.69</td>
<td>1.34:1</td>
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<tr>
<td>MP-RC wash</td>
<td>1.45</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>MP-NC original</td>
<td>23.90</td>
<td>4.29</td>
<td>3.14:1</td>
</tr>
<tr>
<td>MP-NC wash</td>
<td>1.21</td>
<td>1.95</td>
<td></td>
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</table>
decomposition routes of MP-RC and MP-NC. We believe that both are keys to understanding the amorphous phase in the MP-NC sample. First, we have quantified the amounts of surface water and structural water using TGA with a long hold at 100 °C (Figure 4). We use “structural water” here as an umbrella term, keeping in mind that it could also be protons or hydroxyl groups. For MP-NC, the total weight loss is 20%, and 10% happens at 100 °C. For MP-RC, the total weight loss is 12%, and 4% takes place at 100 °C. This indicates that the MP-NC sample has absorbed more total water and also has a larger amount of structural water than the carbon-containing MP-RC.

Second, we took XRD patterns of the compounds after TGA, which are the final decomposition products of MP-RC and MP-NC (Figure 5). Both of them are a mixture of Mn2P2O7 and Mn(PO3)2. The product of MP-RC is majorly Mn2P2O7,7 wt % according to Rietveld refinement, while the product of MP-NC is majorly Mn(PO3)2 (60 wt %). This suggests the existence of two phases in both delithiated products; then Mn2P2O7 is formed from MnPO4 decomposition, as was previously reported,22 and Mn(PO3)2 is due to amorphous phase decomposition. It is also consistent with the element ratio: a mixture of Mn3P2O7 and Mn(PO3)2 would give a Mn/P ratio between 0.5 and 1.

Led by clues that the amorphous phase is likely to be a pyrophosphate and its decomposition products are Mn(PO3)2 and water, we searched the PDF4+ database and identified the most likely candidate as MnHP2O7. We have synthesized this compound as described in the Supporting Information and confirmed that its decomposition product is, in fact, Mn(PO3)2, as was previously reported.29 We then used this MnHP2O7 along with other manganese compounds containing the (pyro)phosphate group and water or protons (MnPO4·H2O and Mn2P2O7; Figure S3) to investigate the amorphous product using local techniques: 31P and 1H NMR and XAS at Mn K-edge.

The 31P NMR resonance frequency is dominated by the Fermi–contact interaction, which is specific to the transition-metal-ion coordination shell around the nucleus.30 The exact shift depends on the transition-metal oxidation state as well as the bond geometry. Furthermore, the resonances are broadened by the dipolar interaction between the unpaired electrons and detected nucleus. This spectral broadening can be
reduced to some extent by MAS by breaking the resonance into an isotropic line and a manifold of spinning sidebands (Figure 6; Hahn echo spectra in black). The 2D projection MATPASS is used here to separate the spinning sidebands from the isotropic resonances, resulting in the isotropic spectrum (Figure 6, red), which can be used to identify 31P in different environments. The 31P NMR spectrum (Figure 6) of MP-RC displays a single resonance at ∼7500 ppm, which is the main PO₄ resonance. The spectrum of MP-NC shows the same environment at ∼7500 ppm as that for MP-RC and a second broad resonance between 3000 and 7000 ppm. The width of this resonance, even in the isotropic spectrum, can be the result of multiple overlapping 31P disordered environments. The region of this broad resonance overlaps with some of the resonances observed for MnHP₂O₇.

The 1H MAS NMR spectra of all samples contain two sharp resonances at 2 and 7 ppm (Figure 7). Because these resonances are very sharp and have relatively long spin–lattice relaxation (about 1 s), we believe that the corresponding H atoms are not coordinated to Mn ions but could be due to some mobile surface species. Additional broader resonances that are also shifted outside the standard chemical shift range of 1H are observed for MnPO₄·H₂O (at ∼9.3 ppm) and MnHP₂O₇ (29 and 15 ppm). These could correspond to nonmobile H atoms in closer proximity to manganese. The 1H NMR spectrum of MP-NC has a broad contribution at 15–30 ppm (above the probe background signal and more clearly seen in the sideband region in the inset), which may be due to the contribution of structural hydrogen in MP-NC and is slightly more significant than that for MP-RC. Thus, 31P and 1H MAS NMR spectra suggest that the amorphous phase in MP-NC is similar to that in MnHP₂O₇. However, because the manganese oxidation state is between 2+ and 3+, MP-NC could be a mixture of MnHP₂O₇ and MnH₂P₂O₇. Figure S4 shows the structures of MnHP₂O₇ and MnH₂P₂O₇.

Furthermore, we have performed a high-temperature in situ XAS experiment on MP-NC to study the phase transformation upon temperature change. Two regions of changes were observed by analysis of Mn K-edge by XAS. The first process (20–100 °C) only involves the elimination of surface ligands, especially the removal of adsorbed water, which is evidenced by the gradual decrease in the intensity of the main absorption peak along with a slight downshift of the edge position as the temperature increases from 20 to 100 °C (Figure 8a). As the temperature rises above 100 °C, temperature-induced transformation in the sample is reflected by spectral changes in Figure 8b. Specifically, the absorption edge shifts to a lower energy accompanied by a significant increase in the intensity of the main absorption peak. This finding by XANES suggests that manganese is being reduced upon heating, and such a reduction of the manganese valence is closely associated with the change of the local environment around the element. On the other hand, the evolution of the manganese local structure caused by thermal treatment is documented in the concurrently collected EXAFS data. Inspecting the radial distribution function of manganese obtained from Fourier-transformed EXAFS, we observe the most noticeable change in the r range of 1–2 Å, where the peak(s) predominantly feature the interaction between manganese and its nearest-neighboring atoms (oxygen). As demonstrated, the split peaks exhibited by MP-NC at 100 °C and lower temperatures gradually converge and eventually at 300 °C become one sharp band at a relatively longer distance.
EXAFS data of the MP-NC sample. Fitting results (Table S2 and Figure S5) reveal that, in the MP-NC sample of 100 °C, manganese is coordinated by oxygen at two different distances: 1.87 ± 0.02 and 2.09 ± 0.03 Å. The calculated coordination numbers (CNs) are 2.4 ± 0.6 and 2.2 ± 0.6, respectively. In contrast, upon thermal treatment, the first coordination shell of manganese in the sample can be characterized by hexacoordinating oxygen (CN = 6.5 ± 0.7) at a distance of 2.10 ± 0.01 Å. For the latter case, a Mn−Mn bond with CN = 2 and the calculated distance of 3.42 ± 0.03 Å, is required to fit the EXAFS data at a higher r range, which is consistent with the proposed structure of Mn(PO3)2. This subtle discrepancy between the two data provides more direct evidence for transformation of the structure.

The spectral features remain the same as the sample is cooled from 300 to 25 °C, indicating an irreversible transformation. In addition, both XANES and EXAFS data of the temperature series exhibit multiple isosbestic points, suggesting chemical transformation is a direct reaction of two phases: MP-NC → Mn(PO3)2. Consistent results were obtained as a linear composition fit (LCF) was applied to XANES and EXAFS data (Figure 8c). One concludes that, with a temperature increase, MP-NC is gradually converted to Mn(PO3)2. The phase transformation completes at a temperature slightly above 200 °C, and no significant change is involved as the temperature is raised further.

As we mentioned before, upon heating, the loss of water leads to structural disorder and phase transformation, which decreases the thermal stability of both MP-RC and MP-NC. However, if we perform the heating process under high vacuum, where surface water has been removed before heating, the thermal stability of MP-RC and MP-NC could be increased.

Figure 8. In situ XAS at Mn K-edge of MP-NC: (a) XANES between room temperature and 100 °C; (b) XANES between 100 and 300 °C; (c) mixing fraction of the start and end phases during thermal treatment of MP-NC. LCF on Mn K-edge: (red) XANES (energy region 6528.5−6578.5 eV); (blue) EXAFS in k space: $k_w = 2$; k range of 3−12.

To further investigate the thermal stability of MP-RC and MP-NC under high vacuum, the XRD and XPS spectra of the samples before and after high vacuum heating are compared. From the XRD data (Figure 9), we can find that the major phase of MP-RC did not change after vacuum heating. However, the relative intensity of the 29° peak (asterisk) increased, which is a characteristic peak of Mn2P2O7. Also, we can see the 29° peak of the MP-NC sample appearing after heating, suggesting that both MP-RC and MP-NC have been partially decomposed upon heating. When the XPS before and after high-vacuum heating (Figure 10) are compared, it can be seen that the Mn2+ peak became stronger in both MP-RC and MP-NC postheating. This indicates that the samples started to decompose and some Mn2P2O7 was formed. The valence band also shows an increase in features associated with the pyrophosphate phase; the most noticeable signature is the...
feature near 15 eV. No change was observed in the C 1s region except for a reduction of the intensity of the surface carbon peaks. Combining the XRD and XPS results, we conclude that both MP-RC and MP-NC partially decompose at 700 °C under high vacuum. This shows that their thermal stability under high vacuum is much higher than that under ambient conditions, considering that the decomposition temperature of MP-RC is only 400 °C in the latter case.

To confirm the thermal stability of MP-RC and MP-NC under high vacuum, we have used high-temperature in situ TEM diffraction to study the phase transformation from room temperature to 800 °C. According to Figure 11, initially MP-NC is amorphous. The first diffraction pattern appears at around 660 °C and is identified as Mn(PO₃)₂. After cooling, the in situ diffraction pattern is also identified as Mn(PO₃)₂, except that the orientation changed. Similarly, SAED shows that the phase of the ex situ heating product is also Mn(PO₃)₂, with single-crystal spot patterns. As the ex situ product is held at 600 °C for 1 h, a higher crystallinity is expected.

Figure S6 shows a typical index diagram of the SAED pattern of MP-RC. In the in situ heating process (Figure 12), the starting material is polycrystalline MnPO₄, and the phase transformation does not occur until about 790 °C, where we first identify a Mn₃P₂O₇ pattern. To avoid the beam effect, diffraction patterns were taken from other areas of the sample, and they confirm the phase transformation, as shown by the diffraction pattern indexed as Mn₃P₂O₇ [001] at 800 °C, which remains stable after cooling. TEM diffraction proves that the in situ heated product is the same as the ex situ heated product.

Finally, putting together the results of various techniques, we propose that, during the chemical delithiation of LiMnPO₄, an amorphous phase is formed, which is a mixture of MnHP₂O₇ and MnH₂P₂O₇ (named as MnHₙP₂O₇, where 1 < n < 2). Such an amorphous phase is formed by the following side reaction:

\[
2\text{LiMnPO}_4 + 4\text{NO}, \text{BF}_3 + (1 + 0.5y)\text{H}_2\text{O} \rightarrow \text{MnH}_3\text{P}_2\text{O}_7 + \text{Mn(NO)}_3 + 2\text{BF}_3 + 2\text{HF} + 0.25\text{yO}_2 + 2\text{LiF} + 2\text{NO}_2
\]

MnH₃P₂O₇ and MnPO₄ are the two end members of the chemical delithiation process. If LiMnPO₄ is well carbon-coated and delithiated under perfect conditions (oxygen- and moisture-free), the product should be pure MnPO₄. However, if LiMnPO₄ is not protected by carbon or delithiated in a relatively high-moisture-level condition, the product would be a...
A mixture of $\text{MnH}_y\text{P}_2\text{O}_7$ and $\text{MnPO}_4$. In the worst case, it becomes completely amorphous $\text{MnH}_y\text{P}_2\text{O}_7$ (MP-NC). Thus, MP-RC ($\text{Mn}_{0.84}\text{PO}_4$) can be considered as major $\text{MnPO}_4$ with minor $\text{MnH}_y\text{P}_2\text{O}_7$, while MP-NC ($\text{Mn}_{0.65}\text{PO}_4$) can be considered as minor $\text{MnPO}_4$ with major $\text{MnH}_y\text{P}_2\text{O}_7$. Thermal decomposition of $\text{MnHP}_2\text{O}_7$ and $\text{MnH}_2\text{P}_2\text{O}_7$ should follow these reactions:

$$\text{MnHP}_2\text{O}_7 \rightarrow \text{Mn(PO)}_2 + 0.25\text{O}_2 + 0.5\text{H}_2\text{O}$$

$$\text{MnH}_2\text{P}_2\text{O}_7 \rightarrow \text{Mn(PO)}_3_2 + \text{H}_2\text{O}$$

The side reaction with water possible upon chemical delithiation compromises the thermal stability of $\text{MnPO}_4$ and possibly its other properties. Even if the XRD pattern of chemically delithiated $\text{MnPO}_4$ shows a pure phase, it possibly contains a certain amount of amorphous-phase $\text{MnH}_y\text{P}_2\text{O}_7$. The easiest test to determine the degree of amorphization is TGA with the following XRD analysis of the products. Residual water present in electrochemical cells is also expected to influence the electrochemical behavior of the LiMnPO$_4$ cathode. On the positive side, we have shown that MnPO$_4$ is much more stable than was previously reported if contact with a humid environment is avoided.

**CONCLUSION**

Analysis of the chemical delithiation products of LiMnPO$_4$ and their thermal decomposition products by XRD, XAS, XPS, and TEM has revealed the mechanism of chemical delithiation of LiMnPO$_4$ and the thermal stability of its products. During chemical delithiation, MnPO$_4$ suffers from a side reaction with residual water in the solvent. This results in structural disorder and partial manganese dissolution into the solvent, eventually leading to amorphization. The extent of this side process depends on the water content and on whether the surface is carbon-coated or not. Carbon-coated LiMnPO$_4$ mostly forms olivine MnPO$_4$ upon chemical delithiation. The amorphous phase prevailing in the delithiation products of noncoated LiMnPO$_4$ has a different composition from olivine MnPO$_4$ and is even more hygroscopic. This amorphous phase is a mixture.
of MnH2P2O7 and MnH2P2O7, and it starts to decompose to Mn3O4 at 100 °C. However, under high-vacuum conditions, both olivine MnPO4 and the amorphous phase show significantly higher thermal stability than that at ambient conditions. Olivine MnPO4 decomposes at 800 °C under high-vacuum conditions, in contrast to the decomposition temperature of 400 °C at ambient conditions, while the amorphous phase decomposes to Mn3O4 at 660 °C. Such increased thermal stability is shown to be related to surface water removal at the high-vacuum condition.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00089.

XRD patterns and Rietveld refinement of LMP-RC and LMP-NC, lattice parameters of LiMnPO4 and MnPO4, XANES spectra of MnPO4 and reference materials, synthesis methods of NMR standards MnPO4, Mn2P2O7, and MnH2P2O7 and their derivatives, and the diffraction patterns, structures of MnH2P2O7, and MnH2P2O7, results of EXAFS analysis of amorphous MnPO4 upon heating, and the typical index diagram of the SAED pattern of MP-RC (PDF).

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Notes
The authors declare no competing financial interest.

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