Supplementary Materials

Contents

Figure S1. The procedure for the preparation of NH$_4$FePO$_4$$\cdot$H$_2$O and the XRD results ...........4

Figure S2. XRD pattern of the 0 hr-sample with and without annealing .................................4

Figure S3. A comparison of the crystal structures of LiFePO$_4$ and NH$_4$FePO$_4$$\cdot$H$_2$O ............5

Figure S4. SEM and TEM images of the 1.5 hr-sample..........................................................6

Figure S5. Low-magnification SEM images of the 2-5 hr samples. .......................................7

Figure S6. Low-magnification SEM images of the 6-15 hr samples. .....................................8

Figure S7. XRD pattern of the LiFePO$_4$ products synthesized without using NH$_4^+$ or citric acid .............................................................................................................................................9

Figure S8. XRD and SEM results of the 120 hr-sample.........................................................10

Figure S9. The electrochemical results of the 0, 1, and 1.5 hr samples.................................11
Preparation of \( \text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O} \)

0.005mol \( \text{NH}_4\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O} \) and 0.005mol \( (\text{NH}_4\text{)}\text{H}_2\text{PO}_4 \) were thoroughly dissolved in 10ml de-ionized water at room temperature to prepare clear \([\text{Fe}^{2+}]\) and \([\text{PO}_4^{3-}]\) solutions, respectively. Then the \( \text{NH}_4\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O} \) and \( (\text{NH}_4\text{)}\text{H}_2\text{PO}_4 \) solutions were mixed under vigorous stirring. The mixed solution was then left to react for at least 30 minutes. After that, the 0.2M ammonia solution was added slowly under vigorous stirring until a pH value of around 7 was obtained. A green slurry was consequently produced. After homogeneously mixing, the slurry was then quickly transferred into an autoclave, which was sealed and put into an oven with a temperature of 160 °C and kept hydrothermal conditions for 5 hours. After the autoclave was naturally cooled to room temperature, the resulting grey-color precipitates were filtered and vacuum dried at 80°C for 12 hours to yield the \( \text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O} \) (NFP) materials. Figure S1 shows XRD pattern of the produced NFP material. The observable reflections can be indexed to single phase of \( \text{NH}_4\text{FePO}_4\cdot\text{H}_2\text{O} \) according to JCPDS-450424.
Figure S1. XRD pattern of the NH$_4$FePO$_4$·H$_2$O (a) before and (b) after being coated with carbon (roughly corresponds to 5 wt% C) and annealed at 600 °C for 2h under 99.995% Ar gas protection. The bottom magenta, red, and green bars signify the observed Bragg reflections from the NH$_4$FePO$_4$·H$_2$O (JCPDS-450424), Fe$_2$P$_2$O$_7$ (JCPDS-761762), and Fe$_3$(PO$_4$)$_2$ (JCPDS-810694) phase, respectively.
Figure S2. XRD pattern of the precursor prior to hydrothermal reaction (0h-sample) (a) before and (b) after calcination at 600 °C for 2h under a mixture of 95 % Ar and 5 % H₂ atmosphere. The bottom green, magenta, and purple bars signify the observed Bragg reflections from the Fe₃(PO₄)₂ (JCPDS-810694), NH₄FePO₄·H₂O (JCPDS-450424), and Fe₃(PO₄)₂·8H₂O (JCPDS-300662) phase, respectively. The red asterisks indicate the unknown phases.
Figure S3. A comparison of the crystal structures of (a), (c), (e) LiFePO$_4$ (S.G. $Pnma$) and (b), (d), (f) NH$_4$FePO$_4$·H$_2$O (S.G. $Pmn2_1$) viewed along different directions. The figures were generated with the VESTA software. 70
**Figure S4.** (a) Low-magnification SEM and (c) TEM images of the product after hydrothermal reaction for 1.5 h, which demonstrate that the particles have an egg-like particle morphology with particle sizes ranging from 1-2 µm. (b) High-magnification SEM image of the egg-like single particle, revealing that the round particles have very rough surface surrounded by ultra-thin plate-like nanocrystallites. The TEM image in (d) focuses on the surface of a single particle, which confirms that the round particle is covered by ultrafine nano-plates with sizes ranging from a few to 100nm. The TEM image in (e) shows a single plate-like nanocrystallite and the inset in (e) shows the corresponding SAED pattern.
Figure S5. Low-magnification SEM images of the products after hydrothermal reaction for (a) 2, (b) 3, (c) 4, and (d) 5 hr.
**Figure S6.** Low-magnification SEM images of the products after hydrothermal reaction for (a) 6, (b) 8, (c) 10, and (d) 15 hours. The inset of (b) shows zoom of the SEM image of one truncated rhombohedra hollow particle.
Figure S7. XRD pattern of the LiFePO₄ products synthesized in the absence of (a) NH₄⁺ and (b) citric acid. The experimental parameters of (a): [FeSO₄] = 0.1 M, [KH₂PO₄] = 0.1 M, [LiOH] = 0.3 M, [CA] = 0.05 M, pH ≈ 7, 180 °C, 15 hr. The experimental conditions for (b): [NH₄⁺] = 0.3 M, [Fe²⁺] = 0.1 M, [Li⁺] = 0.2 M, pH ≈ 7, 180 °C, 15 hr.
Figure S8. (a) XRD pattern and (b) SEM image of the product after hydrothermal reaction for 120 hours.
Electrochemical results of the 0, 1, and 1.5 hr samples

The electrochemistry of the samples collected at the early stages of the hydrothermal reaction and tested as synthesized without carbon coating and annealing (after stabilization for 6 cycles) cycled between 1.5 and 4.2V is shown in Figure S9. For comparison, the result of single phase NH$_4$FePO$_4$.H$_2$O is also included. Note that all the samples have similar voltage profiles with sloping electrochemical processes. But some subtle differences can be observed. A short plateau starts to emerge in the 1.5hr-sample, the material exhibiting only a small polarization and good reversible capacity. NFP has a relatively flat discharge plateau at around 2.2V. Interestingly, the electrochemical voltage profile features changed considerably after the samples had been coated with 5 wt% conductive carbon and annealed at 600 °C for 2 hr in 99.99% Ar inert gas atmosphere as demonstrated in Figure S9 (b). The 0 hr-sample has a long and flat discharge plateau at round 1.8 V and S-shape charge plateau extending from 2.1 V to 2.7 V with the highest reversible capacity of ~125 mAh/g. But the polarization, ~0.4V, is still very large. This electrochemical reactivity toward Li$^+$ insertion and de-insertion may be due to the insertion of Li into Fe$_3$(PO$_4$)$_2$, a thermal decomposition product of the 0 hr-sample (Figure S2). More detailed experiments are in progress to investigate this further. The 1.5 hr-sample shows a much reduced polarization with flat charge/discharge plateau at around 3.45 V, which is characteristic feature of olivine LiFePO$_4$. But the capacity is very limited (~45 mAh/g between 2.5-4.3 V, ~80 mAh/g between 1.5-4.3 V) in comparison to the theoretical capacity of olivine LiFePO$_4$, 170 mAh/g. Noticeably, after annealing, the 1 hr-sample has very similar electrochemical features to the thermal decomposition product of NH$_4$FePO$_4$.H$_2$O except that it also shows a small charge/discharge plateau at around 2.3V.
Figure S9. Galvanostatic voltage profiles (the 6th cycle) of the samples at the early stages of the hydrothermal reaction (a) before and (b) after carbon coating (corresponding to 5 wt% C) plus annealing at 600 °C for 2h in 99.99% Ar gas protection. For comparison, the curve of the annealed NH₄FePO₄·H₂O is also included. The current density was fixed at 17 mA/g.