Wet Mechanical Route To Synthesize Morphology-Controlled NH₄MnPO₄·H₂O and Its Conversion Reaction into LiMnPO₄

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Supporting Information

ABSTRACT: A mechanical route using a grinding apparatus such as a planetary ball mill is a simple and scalable method to produce powder materials. However, the control of the particle shapes is difficult. In this paper, we report a wet mechanical process in water to synthesize NH₄,MnPO₄·H₂O (AmMnP) with various shapes (plates, flakes, rods, and nanoparticles). This process involves planetary ball milling of inexpensive raw materials (NH₄H₂PO₄ and MnCO₃) at room temperature. Morphology-controlled AmMnP particles can be obtained by only adjusting the milling conditions such as milling time, ball size, and centrifugal acceleration. Furthermore, the conversion of AmMnP into LiMnPO₄ with two different approaches (solid-state and hydrothermal reactions) has been investigated to evaluate its future applicability as a cathode for lithium-ion batteries. As a particle synthesis with a unique morphology can be attained based on a dissolution–precipitation mechanism in a solution via a suitable combination of raw materials, the study results will promote wet mechanical processes to be widely used as classic but advanced particle synthesis method.

1. INTRODUCTION

Ammonium transition metal phosphates, NH₄,MePO₄·H₂O (AmMeP, Me²⁺ = Mn, Co, Fe, Ni, Cu), have been widely employed in industrial applications such as fertilizers, pigments, and fire-retardants for a long time.¹⁻³ These constituent elements are an indispensable component for plant growth. Because AmMeP with its layered crystal structure can exhibit ion channels,⁴ recent scientific interest in these materials is toward their functional applications such as supercapacitors and magnetic materials.⁵⁻⁸ The tuning of the constituent metal elements, including a replacement of the NH₄⁺ ions by other monovalent cations, can lead to unique redox reactions. The resulting materials potentially exhibit superior electrochemical performances.

Another important application of AmMeP compounds is as a precursor for the preparation of olivine-type cathodes (e.g., LiFePO₄, LiMnPO₄ (LMP), LiCoPO₄, NaMnPO₄) for lithium/sodium-ion batteries.⁹⁻¹⁴ The topology of the metal phosphate layer in the ac plane of AmMeP matches that in the bc plane of olivine-type LiMPO₄.¹⁵ Therefore, morphology-controlled LiMePO₄ and NaMePO₄ cathodes can be prepared through ion-exchange or calcination reactions. Most approaches for the synthesis of AmMeP particles are based on a precipitation method from aqueous solutions, reported by Bassett and Bedwell in 1933.¹⁶ Zeng et al. developed a general method to prepare multinary metal ammonium phosphate microspheres constructed with nanoflakes grown via a hydrothermal (HT) treatment.¹⁷ The crystal growth of AmMeP in a solution tends to form two-dimensional shapes such as sheets, plates, and flakes owing to the layered crystal structure. In the solution-based synthesis methods, concentrated or strongly basic solutions are often used for the control of the pH value and precipitation of products. Following the increasing demand for environmental-friendly particle synthesis, a milder preparation route using acid–base reactions between solids at low temperatures was reported by Yuan et al.¹⁸,¹⁹ However, the aging time of the mixed powder must cover minimum 12 h because of the slow ion diffusion at the interface.²⁰ Moreover, the solid-state (SS) synthesis restricts the shape control of particles compared with a solution synthesis. The development of a scalable, environmental-friendly, and low-cost synthesis method for morphology-controlled AmMeP particles is crucial not only for the conversion application for olivine-type cathodes but also for the acquirement of a new synthesis strategy for functional particles.

In this paper, we report a wet mechanical process in water to synthesize NH₄,MnPO₄·H₂O (AmMnP) particles with various shapes (plates, flakes, rods, and nanoparticles) using inexpensive raw materials (NH₄H₂PO₄ and MnCO₃). We used a planetary ball mill to effectively prepare products by grinding the raw materials, dissolving them in water, and forcing their precipitation in the solution. Despite the milling process, morphology-controlled AmMnP particles can be

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obtained by adjusting the milling time, ball size, and centrifugal acceleration. The formation mechanism of AmMnP particles via ball milling is discussed based on a dissolution−precipitation mechanism. The advantages brought by a wet mechanical process are mainly that reaction processes from grinding, mixing, and dissolution of starting powders in a solution to precipitation of products are achieved in one step, that fine particles can be obtained while dispersing in a solution, and that a nonequilibrium reaction may occur locally, allowing the formation of metastable materials. Achieving the morphology control of particles by a physical approach such as ball milling in a solution may lead to breakthroughs in particle synthesis of advanced materials. Furthermore, we investigated the conversion reaction of AmMnP into LiMnPO₄ with two different approaches, i.e., solid-state and hydrothermal reactions, to evaluate the inheritance of the particle shape and particle growth through the conversion process.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of AmMnP via Wet Mechanical Process. The planetary ball milling of NH₄H₂PO₄ and MnCO₃ in water was carried out to prepare AmMnP (Figure 1a). Under 10 G and with φ = 2 mm balls, single-phase AmMnP powder was obtained after milling for 3 h. The use of the smallest balls with φ = 2 mm resulted in no precipitates, whereas insoluble MnO₂ still remained after milling. The formation mechanism of AmMnP (milling time, 5 h).

To characterize the AmMnP powder synthesized in the wet mechanical process, FT-IR and TG−DTA measurements were carried out. Figure 1b shows the FT-IR spectrum of the product obtained via milling at 10 G with φ = 2 mm balls for 5 h. The band at 3430 cm⁻¹ corresponded to the O−H stretching vibration of hydrated water molecules, whereas the peak of the bending mode of the O−H group is located at 1637 cm⁻¹. The broad bands below 3235 cm⁻¹ and the bands in the 1400−1500 cm⁻¹ region were attributed to the N−H stretches and N−H bending mode of NH₄⁺, respectively. The sharp bands in the region below 1150 cm⁻¹ corresponded to both the vibrations of PO₄³⁻ and librations of water. All detected bands matched with reported data. Figure 1c shows the TG−DTA curves of the AmMnP powder. The TG curve recorded two-step weight losses with a steep region from 150 to 250 °C and a gradual region up to 550 °C. The weight losses at these steps were 18.4 and 4.6%, respectively. The thermal decomposition of AmMnP consists of the coelimination process of NH₃ and H₂O and the subsequent dehydration condensation.

\[
\text{NH}_4\text{MnPO}_4\cdot\text{H}_2\text{O} \rightarrow \text{MnHPO}_4 + \text{NH}_3 + \text{H}_2\text{O} \quad (1)
\]

\[
2\text{MnHPO}_4 \rightarrow \text{Mn}_2\text{P}_2\text{O}_7 + \text{H}_2\text{O} \quad (2)
\]

These decomposition steps lead to weight losses of 18.9 and 6.0%, respectively. The observed values were close to the theoretical values. We confirm that the thermally treated products at 300 and 500 °C for 1 h were amorphous MnHPO₄ and crystalline Mn₂P₂O₇, respectively (Figure S1). Consequently, AmMnP is first decomposed to amorphous MnHPO₄ phase with an endothermic reaction and is then crystallized to Mn₂P₂O₇.

2.2. Particle Shape Changes through Milling. We investigated the relation between the particle shapes of AmMnP and the milling conditions including centrifugal accelerations, times, and ball sizes. Figure 2 shows the scanning electron microscopy (SEM) images of the AmMnP powders synthesized at 50 G for 2 h with different ball diameters (φ = 1−5 mm). The use of the smallest balls with φ = 1 mm produced nanoparticles with sizes below 100 nm. In contrast, rod-like particles, having a length of a few hundred nanometers to more than 1 μm, were obtained using larger balls of more than φ = 2 mm. The morphology of these products was the
same (Figure 2b−d). The formed rod-like AmMnP particles possessed a gnarled surface and consisted of bundles.

A further widespread synthesis under milling conditions of 10−50 G for 1−5 h with ϕ = 2 and 5 mm revealed the formation of AmMnP with various particle shapes (Figures S2 and S3). Based on the SEM observations, we could create a particle shape diagram. Figure 3 presents the particle shape diagram of AmMnP produced via the wet mechanical process using balls of ϕ = 2 and 5 mm. In the case of ϕ = 2 mm, AmMnP particles with plate/flake shapes were formed under relatively mild milling conditions at a low centrifugal acceleration for a short time. Rod-like particles and nanoparticles were obtained by milling at a higher centrifugal acceleration and for a longer time, respectively. By using ϕ = 5 mm balls, the formation region of AmMnP with plate/flake and rod shapes expanded. Further, AmMnP nanoparticles did not form for milling under 50 G for 5 h. The changing particle shapes from plates to rods during the milling could be observed for products treated with 20 G with ϕ = 5 mm balls. Figure 4a−c shows the SEM images of the AmMnP plates obtained for 1−5 h. The (010) plane of AmMnP was well developed owing to the layered structure. However, the surface of the AmMnP plates became rough with increasing milling time. These plate particles were segmented (like needle ice) from edges during the collisions with balls. The later collected segments exhibited rod shapes. As shown in Figure 2, the use of smaller balls resulted in the formation of nanoparticles. In general, the collision frequency of smaller ball sizes is larger than that of bigger balls. When rod particles receive further mechanical actions via smaller ball sizes or excessive milling, the rod particles will be ground to nanoparticles (Figure 4d). From these results, the mechanism for the change of particle morphology of AmMnP at different milling conditions can be summarized as follows: first, reflecting the layered crystal structure, relatively mild milling conditions at a low centrifugal acceleration for a short time or the use of bigger balls form AmMnP particles with plate/flake shapes. This is probably because the subsequent grinding step after particle formation does not occur yet; second, AmMnP particles formed with two-dimensional morphologies receive a mechanical force with increasing centrifugal acceleration and milling time, resulting in a one-dimensional rod shape. The use of smaller balls is also effective in reducing the particle size. Lastly, relatively severe milling conditions at a high centrifugal acceleration for a long time bring nanoparticles without a specific morphology. Therefore, the formation of AmMnP particles through the wet mechanical process provides shape changes from two-dimensional particles such as plates and flakes to nanoparticles via the grinding of one-dimensional rod particles.

To evaluate the grinding behavior after the formation of AmMnP, we analyzed the specific surface area of the products. Figure 5 shows the specific surface areas of the products obtained by milling for 3 and 5 h with balls of ϕ = 2 and 5 mm. As explained above, the use of smaller balls with ϕ = 2 mm promotes the grinding of the powder, resulting in an increase in the specific surface area. The equivalent particle size can be calculated from the specific surface area (S_w):

\[
d_{BET} = \frac{6}{\rho \cdot S_w}
\]

where \( \rho \) is the theoretical density (2.49 g/cm^3). The AmMnP
particle size of 116 nm at 10 G for 5 h. A different grinding behavior was observed for the φ = 5 mm balls. Although the specific surface area increased with increasing centrifugal acceleration, it showed signs of leveling off at approximately 30 m²/g (80 nm). As shown in Figure 3, the rod shape of the products was maintained. The origin of this behavior can be that the formed rod particles can flow in a relatively large interspace between balls in the solution. By adjusting the milling conditions (centrifugal acceleration, time, and ball size), the synthesis of morphology-controlled AmMnP powders despite a milling process was achieved. Meanwhile, the thermal property did not depend on the particle shape of AmMnP. Although the TG curve shown in Figure 1c was recorded with AmMnP plates, the rod-like particles and nanoparticles exhibited almost the same weight loss behavior except for a low-temperature shift slightly at nanoparticles (Figure S4).

2.3. Formation Mechanism of AmMnP. The formation of AmMnP in the NH₄H₂PO₄ solution was achieved using MnCO₃ as the manganese source; MnCO₃ is insoluble in water (6.5 mg/100 mL) but slightly soluble in an acid solution. The initial approximate pH value of 4.1 for the NH₄H₂PO₄-dissolved solution is a key factor for the dissolution of MnCO₃ and subsequent formation of AmMnP. The dissolution of MnCO₃ caused an increase in carbonate ions in the solution. Accordingly, the pH value of the solution increased with the milling time (Figure S5). The subsequent precipitation of AmMnP occurs via the reaction of NH₄⁺ and MnPO₄⁻ in water. The formation reaction can be described as follows

\[ \text{NH}_4\text{H}_2\text{PO}_4 \rightarrow \text{NH}_4^+ + \text{H}_2\text{PO}_4^- \]  
\[ \text{MnCO}_3 + \text{H}_2\text{PO}_4^- \rightarrow \text{MnPO}_4^- + \text{H}^+ + \text{HCO}_3^- \]  
\[ \text{NH}_4^+ + \text{MnPO}_4^- + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{MnPO}_4\cdot\text{H}_2\text{O} \]  

A key step for producing products via this method is a gradual dissolution process of the raw material in the solution. Recently, we successfully synthesized Li₁.₈₁H₀.₁₉Ti₂O₅·xH₂O and Sr₁₅Al₁₅(OH)₃₄ through the same wet milling method in water. In each case, a combination of water-soluble materials (LiOH and Sr(OH)₂) and insoluble materials (TiO₂ and Al₂O₃) was employed. The insoluble oxides can gradually dissolve in the basic solution in which each hydroxide is dissolved. As the reactant of MnCO₃ is continually supplied by the precipitation of AmMnP, the rate-determining step of the formation of AmMnP is the dissolution of MnCO₃ in water. Further, the grinding of raw materials via wet milling causes an acceleration of the dissolution in the solution. The use of high-energy mills such as a planetary ball mill is suitable for an improvement of the reaction rate.

2.4. Conversion of AmMnP into LiMnPO₄ via Different Approaches. Investigations of the conversion reaction of AmMnP into olivine-type cathodes are crucial for industrial applications of lithium/sodium-ion batteries because battery performances depend on the shapes and structural modifications of cathode particles prepared via different conversion methods. Here, we compared the powder properties of three converted LiMnPO₄ powders originating from AmMnP rod particles: a solid-state reaction with LiOH (SS-LMP); a hydrothermal reaction in an LiNO₃ solution (HT-LMP); and an annealing treatment of HT-LMP (HTA-LMP). Figure 6 shows the Rietveld refinements of the XRD patterns of the three products; LiMnPO₄ was obtained via both conversion routes (solid-state and hydrothermal reactions). Both products exhibited an orthorhombic olivine structure (Pnma). The reaction with lithium sources at high temperatures leads to the formation of impurity phases. The SS-LMP powder in this study also contained tiny amounts of Mn₂O₃ as a byproduct, whereas HT-LMP was phase pure. The Rietveld analysis was carried out for all phases except the impurity phase. Compared with the diffraction peak intensities of SS-LMP and HT-LMP, the (101) and (020)/(211) reflections of SS-LMP were relatively high. Furthermore, sharper diffraction peaks were detected in HT-LMP. The lattice parameters after the refinements are summarized in Table 1. The a-axis of HT-LMP was slightly elongated. These results imply that LiMnPO₄ converted via a solid-state reaction experienced a particle growth at high temperatures. Figure 7 shows the SEM images of the SS-LMP and HT-LMP powders. Although the rod shapes of AmMnP were maintained in both conversion methods, the aspect ratio of the SS-LMP particles seemed to be low. This is caused by a particle growth at high temperatures. The hydrothermal treatment with the Li⁺ solution can cause an ion-exchange reaction of NH₄⁺ thereby maintaining the original particle shape. The plate-like AmMnP particles, in addition, were also converted to LiMnPO₄ while maintaining the particle shape (results not shown). Therefore, a hydrothermal conversion route is suitable for the preparation of olivine cathodes via the conversion of AmMeP with specific particle shapes. Koleva et al. reported that the annealing of LiMnPO₄ converted from AmMnP leads to an anisotropic crystal growth. In this study, the annealing of HT-LMP at 600 °C (HTA-LMP) resulted in an increase in the intensities of the (210) and (020)/(211) reflections (Figure 6c), which resembled the XRD pattern of SS-LMP. Although annealing improves the cation order in crystals after the initial crystallization, a particle growth is inevitable for nanocrystals. Annealing conditions such as temperature and holding time should be controlled to improve the cathode properties while maintaining the particle shape of olivine compounds after a hydrothermal conversion from AmMeP.
4. EXPERIMENTAL SECTION

4.1. Synthesis Procedure of AmMnP. The raw materials NH₄H₂PO₄ (purity: 99.0%; Kanto Chemical Co., Inc., Japan) and MnCO₃ (99.9%; Kojundo Chemical Laboratory Co., Ltd., Japan) were used for the AmMnP synthesis. These powders (3 g; molar ratio of NH₄H₂PO₄/MnCO₃ = 1.2:1) and distilled water (20 mL) were processed in a planetary ball mill (High-G BX254E; Kurimoto, Ltd., Japan). They were put into a stainless steel vessel (170 cm³) with Y₂O₃-stabilized ZrO₂ balls (100 g; diameter, φ: 1–5 mm; Nikkato Corp., Japan). The vessel was sealed and then rotated for 0.25–5 h under centrifugal accelerations of 10–50 G. The centrifugal acceleration was controlled via the revolution speed, and the ratio of rotation/revolution speeds was fixed to approximately 0.5. After the wet milling, the product was collected via centrifugation, washed several times with distilled water, and dried in an oven at 100 °C.

4.2. Conversion of AmMnP to LiMnPO₄. AmMnP with rod shapes was converted to an LiMnPO₄ olivine-type cathode through different approaches: solid-state reaction and hydrothermal reaction.

4.2.1. Solid-State Reaction. The mixture of AmMnP and LiOH·H₂O (>99%; Kanto Chemical Co., Inc.) in a molar ratio of 1:1.15 was prepared by grinding it with an agate mortar and adding a small amount of ethanol. The mixed powder was heated at 500 °C for 2 h under Ar flow. The resulting product was washed with distilled water and ethanol and dried in an oven. The LiMnPO₄ powder converted via the solid-state reaction is denoted as SS-LMP.

4.2.2. Hydrothermal Reaction. The AmMnP powder (0.5 g) and 1 M LiNO₃ (20 mL; Wako Pure Chemical Corp., Japan) were put into a Teflon-lined autoclave (50 cm³) and heated at 120 °C for 6 h under stirring. After the reaction, the product was collected, washed, and dried. This resulting powder is denoted as HT-LMP. Additionally, the HT-LMP powder was annealed at 600 °C for 10 h in air (denoted as HTA-LMP).

4.3. Characterization. The crystalline phases of the products were characterized via powder X-ray diffraction (XRD; D2 PHASER, Bruker AXS K. K., Japan) using Cu Kα radiation generated at 30 kV and 10 mA. The diffraction patterns were acquired with steps of 0.02° (2θ) and a counting time of 1 s/step. The structures of the converted LiMnPO₄ were refined using the Rietveld method with the RIETAN-FP program. The molecular structure of AmMnP was analyzed via diffuse reflectance Fourier transform infrared spectroscopy (FT-IR; IRPrestige-21, Shimadzu Corp., Japan). The powder sample (1 mg) was mixed with dry KBr (100 mg); IR spectroscopy grade, Merck KGaA, Germany) and filled into the sample holder. A thermogravimetric–differential thermal analysis (TG–DTA; TG/DTA6200, SII Inc., Japan) was carried out in air at a heating rate of 5 °C/min. The particle morphology of the products was observed using a field-emission scanning electron microscope (FE-SEM; SU-70, Hitachi Ltd., Japan). The specific surface area of the product was estimated from N₂ adsorption measurements (3Flex, Micromeritics Ltd., Japan). Prior to each measurement, the powder was outgassed under vacuum at 120 °C for 3 h. The specific surface area was calculated via the Brunauer–Emmett–Teller (BET) method.

| sample     | a (Å)   | b (Å)   | c (Å)   | V (Å³) | Rwp (%) | Rp (%) | S       |
|------------|---------|---------|---------|--------|---------|--------|---------|
| SS-LMP     | 10.4503 (27) | 6.1034 (15) | 4.7451 (12) | 302.65 (13) | 7.22 | 5.17 | 1.40    |
| HT-LMP     | 10.4721 (20) | 6.0894 (11) | 4.7652 (9)   | 303.87 (9) | 7.45 | 5.22 | 1.43    |
| HTA-LMP    | 10.4462 (9)  | 6.0977 (6)   | 4.7504 (4)   | 302.59 (5) | 9.02 | 5.35 | 1.69    |

Figure 7. SEM images of (a) SS-LMP and (b) HT-LMP.
Figure S1, XRD patterns of thermally treated products; Figures S2 and S3, SEM images of AmMnP powders obtained via milling at 10−50 G for 1−5 h with Φ = 2 and 5 mm, respectively; Figure S4, TG curves of AmMnP rod-like particles and nanoparticles; Figure S5, pH value of solution during milling (PDF).

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