Carbonate anions controlled morphological evolution of $LiMnPO_4$ crystals†

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$LiMnPO_4$ with a morphology controlled by carbonate anions was prepared *via* a simple template-free hydrothermal reaction; the $LiMnPO_4$ shows a promising electrochemical activity as cathode material for lithium ion batteries.

The synthesis of advanced functional materials with controlled morphology has attracted much attention because the resulting multi-functional materials can be applied in various fields such as batteries, catalysis, electronics, and sensors.[1] A variety of strategies have been attempted to control the morphologies of a broad class of inorganic materials including metals, metal oxides, and many other compounds.[2] In recent years, great interest has been directed toward the lithium-containing compounds due to their potential application as electrode materials in lithium ion batteries.[3] However, the synthesis of morphology controlled lithium-containing compounds is very difficult due to their multicomponent and complex structural chemistry. Until now, there are only few reports on the synthesis of one-dimensional structured lithium transition metal oxides,[4] and templates (including soft and hard templates) were often used to assist their growth.

In several previous reports,[5] one-dimensional rod-like growth in cobalt basic salts was proposed to be connected with the inhibition effect of CO_3^{2-}, which is, however, rarely observed in other compounds. Then, a question arises: is such an effect applicable to other compounds? To address this question, new experimental demonstrations should be explored. Herein we report, for the first time, on one-dimensional rods of a quaternary compound $LiMnPO_4$ fabricated *via* a hydrothermal method that involves the effect of CO_3^2 inhibition. $LiMnPO_4$ is one of the members of the phospho-olivines $LiMPO_4$ (M = Mn, Fe, Co and Ni), with an orthorhombic structure, which are now recognized as attractive electrode materials for lithium ion batteries due to their low cost, nontoxicity, environmental friendliness, and high safety.[3a,b,6,7] Our results indicate that the effect of CO_3^{2-} inhibition may be extended to the fabrication of other one-dimensional objects, and also provide a new way to synthesize morphology controlled lithium-containing compounds.

In a typical process, the chemicals $Li_2SO_4{\cdot}H_2O$ (0.011 ~ 0.03 mol), $MnSO_4{\cdot}H_2O$ (0.02 mol), $NH_4H_2PO_4$ (0.02 mol), and urea ($(NH_2)_2CO$, 0.047 mol) were dissolved in 40 mL distilled water at room temperature. Urea was used to adjust the pH value of the solution since an alkaline condition is necessary to precipitate $LiMnPO_4$.[7b,8] The obtained solution was transferred into Teflon-lined stainless steel autoclaves and heated at 200 °C for 10 h. The precipitated products were filtrated, washed several times with distilled water and finally dried at 120 °C for 10 h.

Powder X-ray diffraction (XRD) patterns of the products were recorded on apparatus (DMAX2500, Rigaku) using Cu Kα radiation to identify the crystalline phase. Fig. 1 shows the XRD patterns of the products prepared with different amounts of lithium. All patterns were identified as orthorhombic structures with space groups of *Pnma*. It is noted that the (020) diffraction peaks gradually became stronger in intensity with a decreasing amount of lithium, and the samples prepared using a slight excess of lithium exhibited an abnormally strong intensity for the (020) diffraction peak as compared to that of the standard pattern (JCPDS No. 33-0804). These changes may imply the anisotropic growth of $LiMnPO_4$ crystals that occurred under the present preparation conditions.

Morphology of the products was observed using scanning electron microscopy (SEM, JEOL, JSM-5600 LV). Fig. 2 shows the SEM images of the products prepared with two different lithium amounts. Different morphologies were observed. For the sample prepared in a solution with a 10% excess of lithium, a rod-based sheet-like $LiMnPO_4$ structure

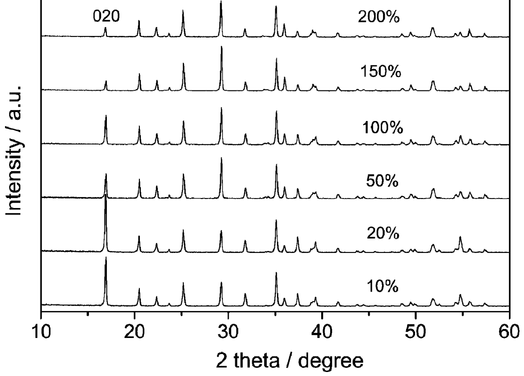

Fig. 1 XRD patterns of $LiMnPO_4$ prepared with a 10–200% excess of lithium. Urea was used to adjust the pH value of the solution.

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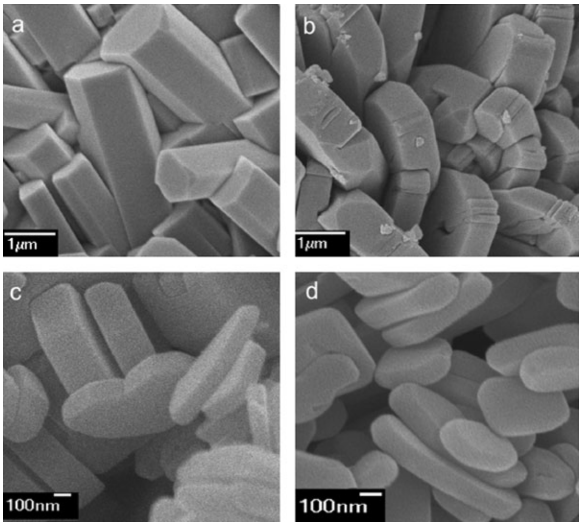

Fig. 2 SEM images of $LiMnPO_4$ prepared under different conditions: (a) urea, 10% excess of lithium, (b) urea, 200% excess of lithium, (c) ammonia, 10% excess of lithium, and (d) ammonia, 200% excess of lithium.

was observed (Fig. 2a and Fig. S1a, ESI†), while the morphology of the $LiMnPO_4$ transformed into a plate-based flower-like structure in the case of a 200% excess of lithium (Fig. 2b and Fig. S1b, ESI†). Such a morphological change was accompanied by a variation in the intensity of the (020) diffraction peak in the XRD pattern. Therefore, the intensity of the (020) diffraction peak may be used as an indicator for the preferential crystal growth of $LiMnPO_4$. From these observations, it is clear that the morphological change of the products is closely associated with the lithium amount in the initial solution.

What is, then, the origin of the morphological change of $LiMnPO_4$? Based on the previous works,[5] the carbonate anions could act as an inhibitor that selectively decreases the rate of crystal growth in the direction of the side planes of the rod. For example, the homogeneous precipitation method using urea generated cobalt compounds in the shape of nanorods in a closed system, while the samples obtained in an open system had platelet-like morphology.[5a] This has been attributed to the fact that the amount of carbonate anions in a closed system during the urea decomposition is greater than that in the open system, from which the carbonate group was released in the form of gaseous CO_2. Such an effect of CO_3^{2-} inhibition could be applied to explain the rod-like growth of $LiMnPO_4$ in the present work. On heating the solution, urea hydrolysis could liberate ammonium and hydroxyl ions, and thus the solution finally achieves an alkaline condition which is needed to precipitate $LiMnPO_4$. Meanwhile, urea hydrolysis in the neutral and basic media could also provide the carbonate ion.[5a] It is well known that lithium carbonate has a very low solubility in aqueous solution. Thus, in the case of a large excess of lithium in the solution, the hydrolysis CO_3^{2-} would be instantaneously precipitated in the form of lithium carbonate, and the crystals of $LiMnPO_4$ grown into a plate form, derived from its intrinsic anisotropic crystal structure without (adequate) CO_3^{2-} inhibition.[9] In the case of a small excess of lithium in the solution, most hydrolysis CO_3^{2-} anions still existed in the solution and could selectively decrease the rate of crystal growth in the direction of the side planes of the rod, ultimately resulting in the rodlike growth of $LiMnPO_4$ crystals. Further, when the synthesis was performed in degassed water or under a CO_2 atmosphere, no apparent changes were observed in the morphology of $LiMnPO_4$ (Fig. S2 and S3, ESI†). Therefore, the morphology of $LiMnPO_4$ can be effectively tuned by simply adjusting the amount of lithium to control the amount of carbonate anions in the solution.

In order to confirm the mechanism proposed above, two sets of independent experiments were conducted where ammonia ($NH_3{\cdot}H_2O$, 25%) instead of urea was used to vary the pH value of the solution, while other conditions were kept. The XRD patterns of the obtained products were very similar (Fig. 3), and the intensity of the (020) diffraction peak was almost unchanged with variation of the lithium amount in the solution, indicative of no morphological changes occurring according to the above observation. This conclusion was confirmed from SEM images of the obtained products (Fig. 2c and d) where only plate-like crystals were observed regardless of the lithium amount in the solution since ammonia can not supply carbonate anions. To get further substantiation, we added ammonium bicarbonate into the reaction system where ammonia and a 10% excess of lithium were used (other conditions were kept the same). The obtained $LiMnPO_4$ showed a rod-like growth (Fig. S4, ESI†) due to the inhibition of CO_3^{2-} that was sufficiently supplied by ammonium bicarbonate. On the basis of these experimental results, it is demonstrated that the morphological transformation of $LiMnPO_4$ from two-dimensions to one-dimension was indeed determined by the inhibition of CO_3^{2-}. In addition, no superstructure was observed in the $LiMnPO_4$ prepared using ammonia, which indicated that the superstructure observed in the $LiMnPO_4$ is related to the use of urea, as observed in other compounds.[5a,c,11]

$LiMnPO_4$ has been studied as cathode material for lithium ion batteries, but electrochemically active $LiMnPO_4$ is difficult to achieve due to its poor inherent electronic conductivity.[6,10] Here, the electrochemical performance of the prepared

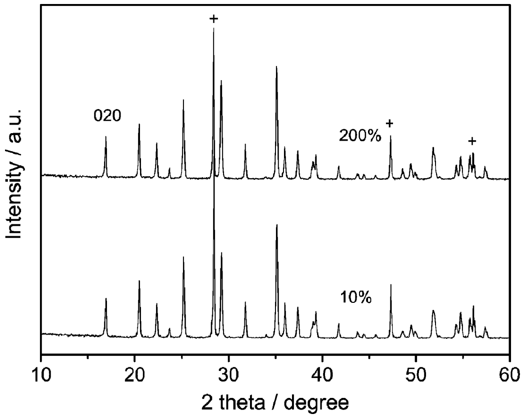

Fig. 3 XRD patterns of $LiMnPO_4$ prepared with a 10 and 200% excess of lithium. Ammonia ($NH_3{\cdot}H_2O$, 25%) was used to adjust the pH value of the solution. The symbol "+" denotes the internal standard silicon.

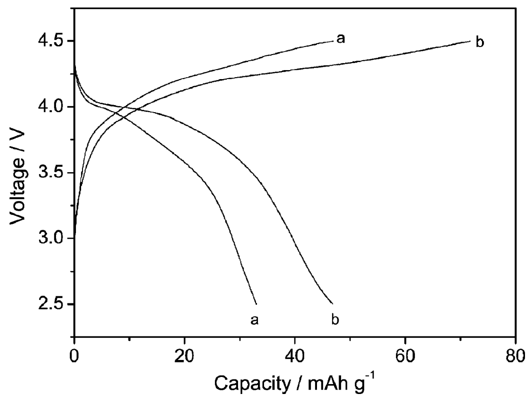

Fig. 4 Charge–discharge curves of $LiMnPO_4$ prepared with a 10% excess of lithium, using urea (a) and ammonia (b) to adjust the pH value of the solution. The current density is 5 mA g^{-1}.

$LiMnPO_4$ was preliminarily evaluated using a 2025 coin-type cell. Fig. 4 shows the charge–discharge curves of $LiMnPO_4$ cycled between 2.5 and 4.5 V at a current density of 5 mA g^{-1}. As can be seen in Fig. 4, the prepared $LiMnPO_4$ clearly exhibited an electrochemical activity with charge and discharge plateaus around the voltage of 4.1 V *vs.* Li^+/Li. These plateaus correspond to the redox of Mn^{3+}/Mn^{2+} that accompanies lithium ion extraction and insertion in $LiMnPO_4$.[7] Similar to the previous reports,[7b,c] the reversible capacity of the prepared $LiMnPO_4$ is much lower than its theoretical value, even though a low charge–discharge rate was applied. This limited capacity is the result of extremely low intrinsic electronic conductivity and slow lithium diffusion kinetics within the $LiMnPO_4$ grains.[7c] Fig. 4 also showed that small particles of $LiMnPO_4$ (obtained using ammonia to adjust the pH value of the solution, Fig. 4b) resulted in lower total polarization and larger reversible capacity than bigger particles obtained using urea, which is consistent with the previous work.[7b,d] Further work for tailoring the preparation of small particles of $LiMnPO_4$ (especially in the case of using urea to adjust the pH value of the solution) is in progress. Anyway, the above results demonstrate that the prepared $LiMnPO_4$ show promising electrochemical activity.

In a conclusion, a facile one-pot route was explored to synthesize shape controlled $LiMnPO_4$. The morphology transformation of $LiMnPO_4$ from two-dimensions to one-dimension was directed by carbonate anions in the solution. As a cathode material for lithium ion batteries, the prepared $LiMnPO_4$ clearly showed an electrochemical activity.

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