

A new strategy to hydrothermally synthesize olivine phosphates

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Experimental

All chemicals (Purchased from China National Pharmaceutical Group Co., Ltd.) of Li source ($\text{LiOH}\cdot\text{H}_2\text{O}$ ($\geq 95\%$)), M source ($\text{MnSO}_4\cdot\text{H}_2\text{O}$ ($\geq 99\%$), $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ ($\geq 99\%$), $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ ($\geq 99\%$)), P source (K_2HPO_4 ($\geq 98\%$), $(\text{NH}_4)_2\text{HPO}_4$ ($\geq 99\%$), H_3PO_4 (85% solution)) and pH regulator (NaOH ($\geq 96\%$), KOH ($\geq 85\%$), $\text{NH}_3\cdot\text{H}_2\text{O}$ (25% solution)) were of analytical grade and used as received in the synthesis experiments. Taking hydrothermal synthesis of LiFePO_4 and LiMnPO_4 from the reaction system with 100 at.% P excess for example, in a typical process, K_2HPO_4 solution (60 mmol (10.45g) K_2HPO_4 dissolved in 20 ml distilled water) and $\text{LiOH}\cdot\text{H}_2\text{O}$ solution (30 mmol (1.26g) $\text{LiOH}\cdot\text{H}_2\text{O}$ dissolved in 20 ml distilled water) was dropped into metal sulfate solution (30 mmol (8.34g) $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$ or (5.07g) $\text{MnSO}_4\cdot\text{H}_2\text{O}$ dissolved in 20 ml distilled water) in sequence under vigorously stirring, and subsequently the formed precursor suspension was stirred for 1 h, then

transferred into a 100 mL Teflon-lined stainless steel autoclave and heated at 200 °C for 10 h. The preparation and transfer of precursor suspension for hydrothermal reaction was performed under N₂ atmosphere. After cooling, the precipitated products were filtered, fully washed by deionized water, and finally dried at 80 °C in vacuum. The yield of LiFePO₄ and LiMnPO₄ was similar (93 - 94 wt.%). In comparative experiments, when H₃PO₄ was selected as P source, a certain amount of NaOH, KOH or NH₃·H₂O solution was added to regulate pH value of the reaction suspension. In addition, LiMn_{0.8}Fe_{0.19}Mg_{0.01}PO₄ was also synthesized by a conventional hydrothermal method from the suspension with 200 at.% Li excess using K₂HPO₄ as P source for comparison. The hydrothermally synthesized LiMPO₄ was ball-milled with 10 wt.% sucrose for 1 h and then annealed at 800 °C under N₂ atmosphere for 1 h. After furnace cooling, the obtained product was LiMPO₄/C composite with a carbon content of ~ 4.8 wt.%.

The crystalline phase of the obtained samples was identified by X-ray diffraction (XRD) on apparatus (D/MaX-3B, Rigaku) using Cu K_α radiation. Materials morphology and particle size were observed by scanning electron microscopy (SEM, XL30, Philips). The carbon content was measured by an elemental analyzer (VarioEL III, elementar, Germany).

Electrochemical performance of samples was evaluated using CR2025 coin-type cell. The cathode was made by mixing LiMPO₄/C composite, super P and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1 in N-methyl pyrrolidinone (NMP) to form homogenous slurry. Then the slurry was coated on an aluminum foil by a doctor blade coater and dried at 100 °C for 10 h in vacuum. The test cell consisted of cathode and lithium foil anode which were separated by a porous polypropylene film and electrolyte of 1 M LiPF₆ in EC : EMC : DMC (1 : 1 : 1 in volume). All cells were assembled in an argon-filled glove box. Cells were charged and discharged using a battery test system (Land

CT2001A) at 30 °C.

Supplementary figures

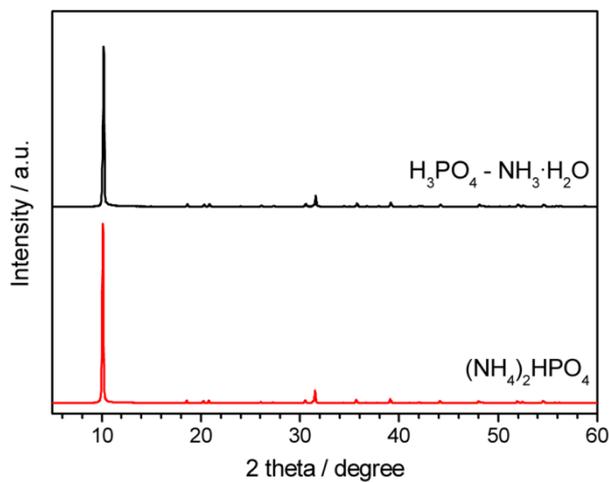


Fig. S1 XRD patterns of the precipitates collected from the precursor suspension with 20 at.% P excess using $(\text{NH}_4)_2\text{HPO}_4$ and H_3PO_4 as P source for hydrothermal synthesis of LiMnPO_4 , respectively.

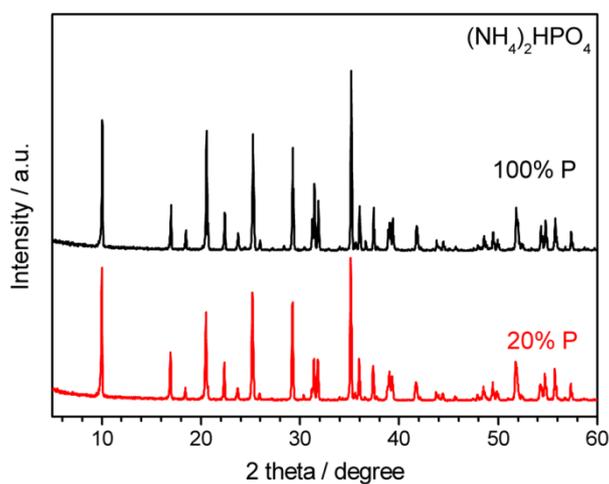


Fig. S2 XRD patterns of LiMnPO_4 hydrothermally synthesized from the suspension using $(\text{NH}_4)_2\text{HPO}_4$ as P source with 20 at.% and 100 at.% P excess, respectively.

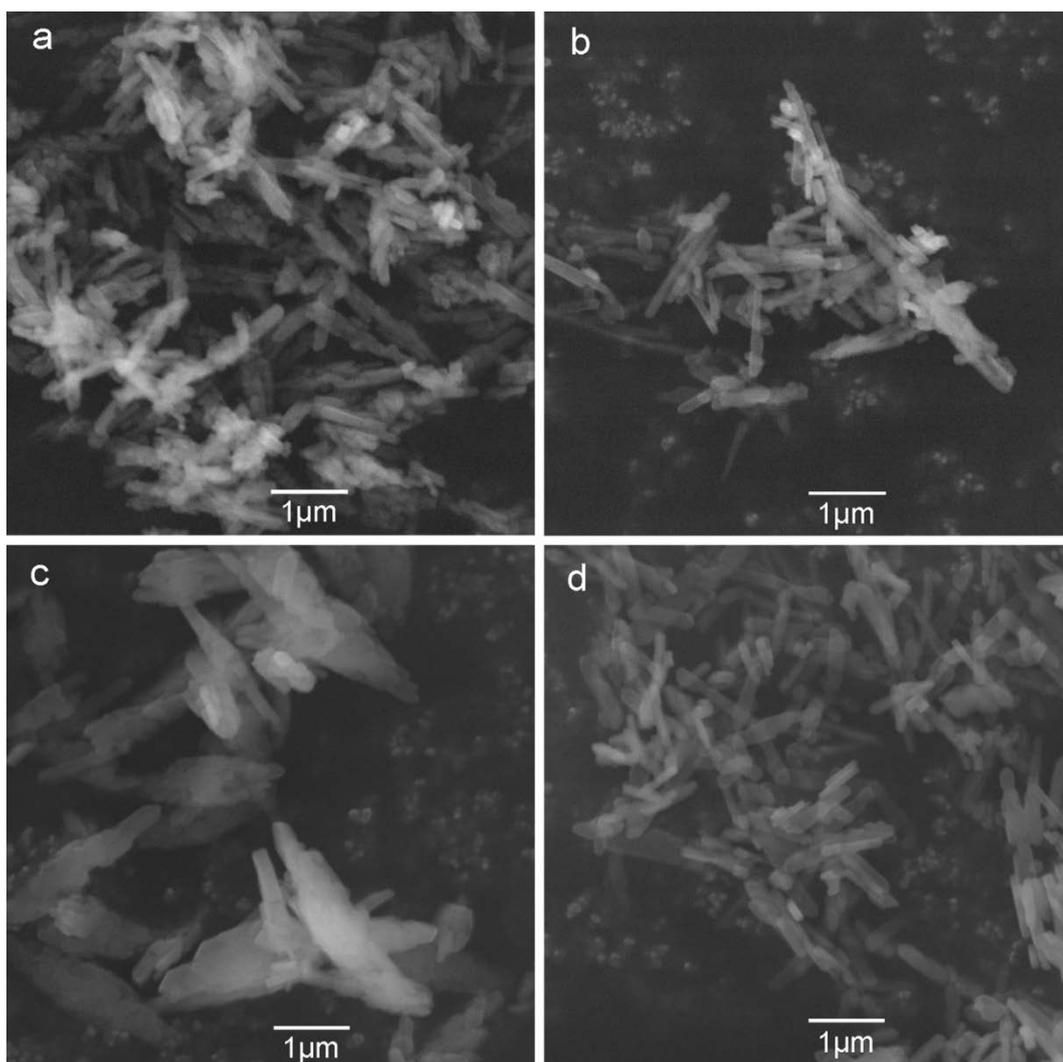


Fig. S3 SEM images of the products hydrothermally synthesized from the suspension using K_2HPO_4 as P source: (a) LiFePO_4 and (b) LiMnPO_4 with 100 at.% P excess, (c) LiFePO_4 and (d) LiMnPO_4 with 20 at.% P excess.

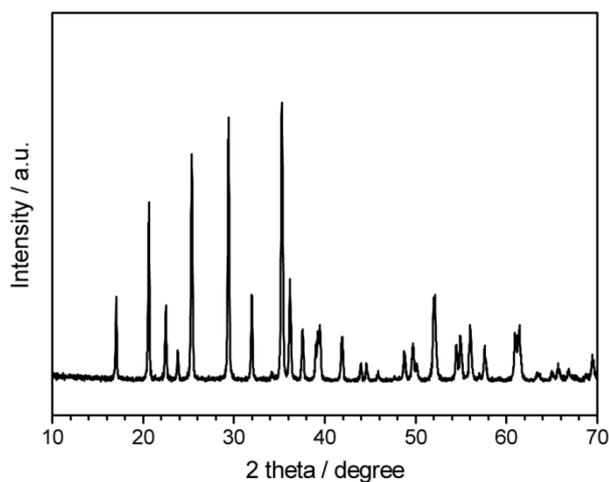


Fig. S4 XRD pattern of $\text{LiMn}_{0.8}\text{Fe}_{0.19}\text{Mg}_{0.01}\text{PO}_4$ hydrothermally synthesized from the suspension with 100 at.% P excess using K_2HPO_4 as P source.

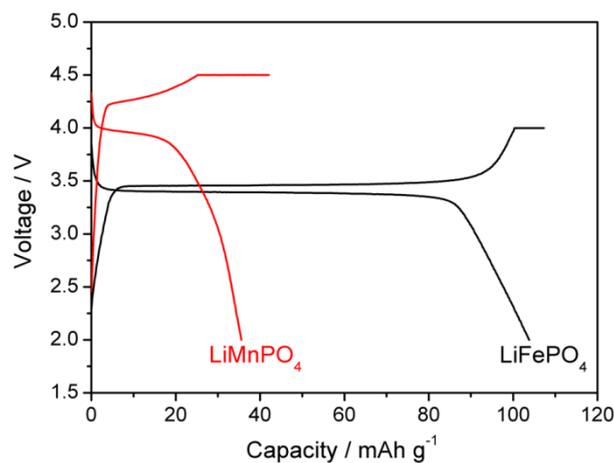


Fig. S5 Typical charge-discharge curves of LiFePO_4 and LiMnPO_4 hydrothermally synthesized from the suspension with 10 at.% P excess using K_2HPO_4 as P source. Cells were charged at 0.1 C to 4.0 V (LiFePO_4) or 4.5 V (LiMnPO_4), held at 4.0V or 4.5 V until the current decreased to 0.01 C and then discharged at 0.1 C to 2.0 V.