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Preparation of $FePO_4$ nano-particles by coupling fast precipitation in membrane dispersion microcontactor and hydrothermal treatment

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HIGHLIGHTS

- A new and simple coupling technique for fabricating nanosized iron phosphate is reported.
- Iron phosphate prepared is about 59 nm and performs excellent in monodispersity and purity.
- A mechanism is proposed to include co-precipitation of nanosized precursors and in situ hydrothermal conversion.
- The micromixing performance during fast precipitation shows critical effect on the morphology of product.

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ABSTRACT

In this work, a new and simple synthesis route for preparing nanosized iron phosphate with high purity under mild conditions was proposed by coupling fast precipitation and hydrothermal treatment. The fast precipitation between $Fe(NO_3)_3$ (with phosphoric acid addition to suppress Fe^{3+} hydrolysis) and $(NH_4)_3PO_4$ was carried out in membrane dispersion microcontactor to obtain precursors having narrow size distribution around 50 nm and containing of $FePO_4$ and $Fe_2(HPO_4)_3$ exclusively. In situ hydrothermal treatment for 1 h in sequence converted $Fe_2(HPO_4)_3$ to $FePO_4$ and initiated the growth of the original $FePO_4$ particle in precursor. Characterizations of the final product by TEM, XRD, TG/DTA and ICP-OES confirmed it was nanoparticles with iron phosphate hydrate with high purity, well dispersion and narrow size distribution around 59 nm. This coupling process is expectable to be controllable, facile and easy to scale up for nanosized $FePO_4$ production with respect to catalysts, cathode and anode materials.

1. Introduction

The ever growing demand for portable batteries with high energy density is exerting pressure on the development of advanced lithium-ion batteries [1]. Olivine $LiFePO_4$, as the most potential candidate of cathode material, is gaining more and more research interest because of huge advantage in cost, safety, naturally abundance and cycling performance. However, $LiFePO_4$ is suffered from its low electronic conductivity at ambient temperature [2,3]. Several ways have been proposed to promote the $LiFePO_4$ electrochemical properties, including rising cell operation temperature [4], carbon coating [5] and minimizing particle size [6–8]. Among them, small particle size is found the most critical and useful way for assuring high performance of $LiFePO_4$ cathode material [1].

The morphology and size of $LiFePO_4$ particles depends on the morphology and size of $FePO_4$ particles during solid-state reaction process [9]. Besides, existence of impurities will lower its electrochemical performance of $LiFePO_4$ [2]. Thus, as the start material for $LiFePO_4$, the preparation of iron phosphate nanoparticle with good monodispersity, small size and high purity is one of the key points to realize of excellent electrochemical performance of $LiFePO_4$.

Various synthetic routes have been reported for preparing iron phosphate [10–13]. However, complex process and low production rates are common problems to many of these techniques. As mostly reported in literatures, iron phosphate is usually synthesized by precipitation with adding a solution of phosphate to a solution of an iron(III) salt. Since Fe^{3+} is prone to hydrolysis, the precipitation has to be carried out under very low pH condition, which makes the procedure time consuming, even up to a week [14]. Due to the long reaction time, the reactant concentration must be very low to prevent the growth and agglomeration of $FePO_4$ particles, which commonly reported low to 0.1 mM [15]. Thus, widely industrial scale production is strictly limited. Some ideas are proposed to overcome these disadvantages, such as adding templates into the reaction system to increase the local concentration near the

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