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Controllable synthesis of Li_3PO_4 hollow nanospheres for the preparation of high performance $LiFePO_4$ cathode material

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ABSTRACT

Lithium phosphate hollow nanospheres were prepared in a membrane dispersion microreactor using aqueous phosphoric acid and lithium hydroxide solutions as reactants. The influences of reactant flow rate ratio and temperature on the purity and morphology of the prepared nanospheres were investigated using X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The results showed that nanospheres prepared in the continuous flow condition had a hollow interior structure with high crystallinity. A possible mechanism for the formation of this hollow structured Li_3PO_4 was also proposed. Using Li_3PO_4 hollow nanospheres as the precursor, $LiFePO_4$ hollow nanospheres were successfully synthesized via a solvothermal route in ethylene glycol. After coating with carbon, the $LiFePO_4$/C hollow nanospheres exhibited excellent electrochemical performance, especially at high rates, and could discharge124 mAh/g at 10 C, and even 98 mAh/g at 40 C.

Introduction

Lithium phosphate (Li_3PO_4) is a multifunctional inorganic material widely used in fields including catalysis, sensors, and lithium batteries. For example, it is known to be a particularly active catalyst for the isomerization of certain alkylene oxides, especially propylene oxide (Ma, Si, Wu, & Zhong, 2011). High yields of unsaturated ethers can also be readily obtained from acetals using an alkaline lithium phosphate catalyst (Rojas, De Vidales, Delgado, & Sinisterra, 1993). Additionally, Li_3PO_4 has been considered as a solid electrolyte for CO_2 gas sensors (Kim, Yoon, Park, & Kim, 2001; Lee & Akbar, 2014; Lee, Dutta, Ramamoorthy, & Akbar, 2006; Noh, Satyanarayana, & Park, 2005; Satyanarayana, Choi, Noh, Lee, & Park, 2007; Wang, Ren, Zhang, Sun, & Jiang, 2012) that also could be used as optical humidity sensors (Zhang, Chen, Yang, & Peng, 2011). The most important application of lithium phosphate lies in the field of lithium batteries. For example, lithium phosphate film doped with nitrogen is the most widely used electrolyte membrane in solid-state thin film lithium batteries (Rabaâ & Hoffmann, 1999). It is also a stable lithium ion conducting solid electrolyte, because stable P=O bonds facilitate the ionic diffusion of Li^+ in the interface between the cathode and electrolyte. Li_3PO_4-based coating materials are also believed to considerably enhance the electrochemical performance of electrode materials for lithium-ion batteries, giving them greater stability and cyclability (Chong et al., 2014; Zhao, Ding, Wang, Li, & Nan, 2013).

Additionally, Li_3PO_4 is broadly used as a precursor for the preparation of phosphate-based cathode materials as lithium battery technology has developed in recent years (Lee, Kim, & Song, 2010; Yang et al., 2013). The reasons for this are easy to understand. First, Li_3PO_4 is a Li-rich and phosphate-containing compound. Thus, it is an excellent candidate for the preparation of phosphate-based cathode materials such as $LiMPO_4$ (M = Fe, Mn) (Xu, Ching, & Chiang, 2004). Second, Li_3PO_4 possesses a Pnma orthorhombic space group, which has been shown to be electrochemically active. In this regard, Li_3PO_4 is an ideal raw material for the preparation of phosphate-based cathode materials because it enables much easier structural transformation. For example, using Li_3PO_4 nanorods and $MnSO_4{\cdot}H_2O$ as the precursors, Yang et al. (2012) synthesized $LiMnPO_4$ nanomaterials with good electrochemical performance through a simple one-pot solvothermal approach.

However, phosphate-based cathode materials have suffered from poor conductivity and lithium mobility. An effective solution may be found through structural design. Hollow spherical materials are quite attractive for improving the electrochemical performance of lithium-ion batteries in terms of the following factors (Hu, Ding, & Li, 2011; Lou, Archer, & Yang, 2008; Luo, Cheng, & Xia, 2007). First, hollow structures would have larger specific surface area and

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lead to better contact with the electrolyte. Second, the thin shell of the hollow structures could reduce the effective lithium-ion diffusion distance, leading to better rate capability. Third, the cavities in the hollow structures would provide extra space for the storage of lithium ions, and thus enhance the specific capacity of the battery. Fourth, the void space of the hollow spherical structures would act as a buffer layer to alleviate the volume expansion of the electrode during Li-ion insertion/extraction, hence improving its cycling performance.

However, only a few studies have been made on the morphological and structural control of hollow Li_3PO_4. For example, Pei, Chen, and Zhang (2012) synthesized hollow Li_3PO_4 particles with an average diameter of about 0.58 μm in a mixed solvent system of glycol and water at 140 °C for 20 h. Zhang et al. (2011) prepared Li_3PO_4 with PVP in a LiOH solution as template for the formation of hollow structures. At present, the preparation of Li_3PO_4 nanospheres with good monodispersity by a fast precipitation method in a short reaction time and simple reaction medium is still difficult. Therefore, it is of great importance, but a challenge, to develop a facile method to synthesize Li_3PO_4 hollow nanospheres.

In recent years, microfiltration membrane dispersion reactors, which have excellent mixing behavior, continuous production, and low equipment cost, have been successfully used to prepare nanoparticles (Luo, Du, Wang, Lu, & Xu, 2011). With the help of their excellent ability of controlled micromixing, these microreactors enable the fast preparation of nanoparticles with controlled morphology and particle size. In our previous study, microreactors have been successfully developed to prepare various nanoparticles, including $CaCO_3$, $FePO_4$, and Li_2CO_3, either in homogeneous or in heterogeneous mixing systems (Du, Wang, & Luo, 2013; Lu, Liu, Zhou, & Luo, 2014; Lu, Zhang, Liu, & Luo, 2012; Wang, Wang, Chen, Luo, & Wang, 2007).

In this study, a new process for the preparation of Li_3PO_4 hollow nanospheres using a membrane dispersion microreactor was developed. Aqueous solutions of lithium and phosphorous sources were mixed continuously in the membrane microreactor to uniformly generate a nanosized precipitate suitable for use as a cathode material precursor. No other surfactant or template was used, and Li_3PO_4 hollow nanospheres were obtained. The operating parameters were optimized and their influence on the morphology and particle size was investigated. A possible mechanism for the formation of the hollow structures is also proposed. To the best of our knowledge, this membrane dispersion reactor synthesis route represents a novel method for the production of a new structure of Li_3PO_4. The obtained hollow Li_3PO_4 nanospheres, which had a diameter of ~200 nm, were used as a precursor to synthesize $LiFePO_4$ cathode material by a simple solvothermal method using $FeCl_2{\cdot}4H_2O$ as the ferric source in ethylene glycol (EG) medium. The obtained $LiFePO_4$ was further coated with carbon by thermal decomposition of sucrose in Ar atmosphere. Compared with those of non-hollow reference $LiFePO_4$/C particles, the $LiFePO_4$/C hollow nanospheres exhibited a much superior rate and cycling performance.

Experimental

Apparatus

Fig. 1 shows the experimental setup. The membrane dispersion microreactor primarily consists of two stainless steel sample plates (50 mm × 50 mm × 18 mm) patterned using laser etching techniques and a stainless steel microfiltration membrane. The stainless steel microfiltration membrane has a pore size of 5 μm and is used as the dispersion medium. The active area of the membrane is 12.5 mm^2, and the geometric size of the microchannel is 15 mm × 0.5 mm × 0.5 mm (length × width × height).

Method

Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$) (98%) and phosphoric acid (H_3PO_4) (85% aqueous solution) were purchased from Alfa Aesar (China) Chemical Co. Ltd., Shanghai, China. Ferrous chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$), ethylene glycol (EG) and sucrose ($C_{12}H_{22}O_{11}$) were purchased from Xilong Chemical Co., Ltd., Guangzhou, China. All of them were of analytical grade. Lithium phosphate (Li_3PO_4, 99%) was purchased from Aladdin Industrial Co. Ltd., Shanghai, China.

Lithium hydroxide monohydrate ($LiOH{\cdot}H_2O$) and phosphoric acid (H_3PO_4) were separately dissolved in deionized water. The concentration of the LiOH continuous feed solution was 3.0 mol/L, and the concentration of the H_3PO_4 dispersed feed solution was 1.0 mol/L. The H_3PO_4 solution was pressed through the membrane into the microchannel to mix with the LiOH solution coming from the continuous feed inlet. The two solutions were mixed at a specified temperature in the microchannel at a flow rate of 50 mL/min each to immediately generate a precipitate. The flow ratio of the

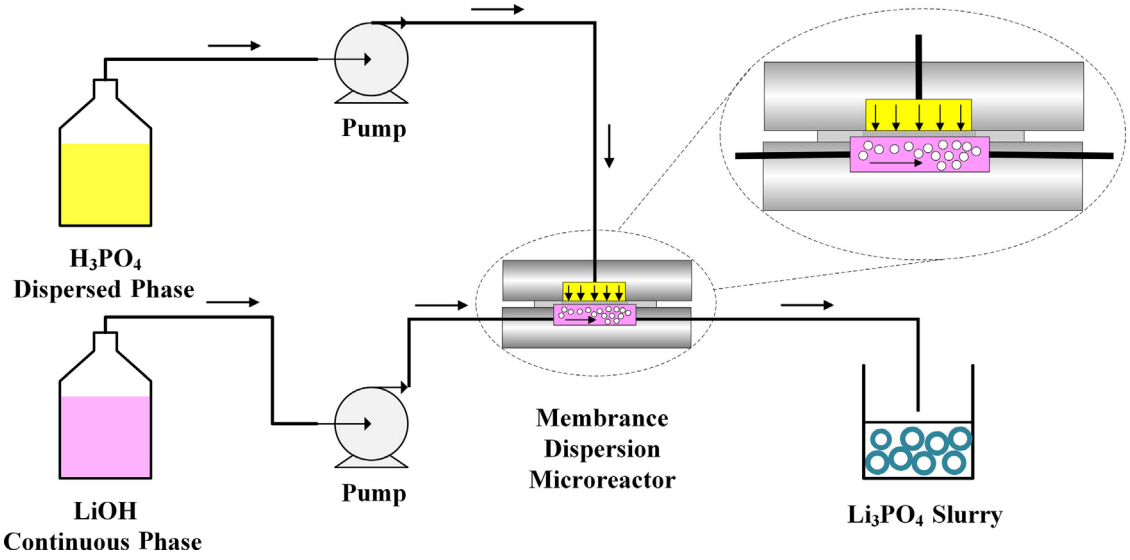

Fig. 1. Experimental setup used to prepare Li_3PO_4 hollow nanospheres.