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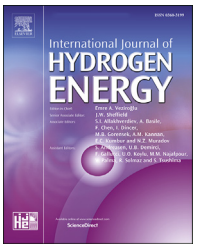

A facile ultrasound assisted high temperature ball milling synthesis of $LiFePO_4$/graphene with enhanced electrochemical performance

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ABSTRACT

$LiFePO_4$/graphene ($LiFePO_4$/G) cathode material was prepared by a facile ultrasound assisted high temperature ball milling method. Ultrasound assisted was found to be effective to promote the dispersing of the precursor in solution. Physical and electrochemical properties of $LiFePO_4$/G were studied. The results exhibited that graphene combined with the $LiFePO_4$ clusters giving rise to a conductive network. $LiFePO_4$/G displayed a well-crystallized $LiFePO_4$ structure and excellent electrochemical performance. The initial discharge capacities of $LiFePO_4$/G were 162.8, 156.8, 151.9, 145.8, 137.5 and 121.6 $mAhg^{-1}$ at rates of 0.1, 0.5, 1.0, 2.0, 5.0 and 10 C, respectively. Moreover, at 0.1 C-rate, the capacity was 160.4 $mAhg^{-1}$ over 100 cycles with a capacity retention of 98.5%. It is concluded that graphene is a conductive additive which can enhance the electrochemical properties of $LiFePO_4$.

Introduction

$LiFePO_4$ material for lithium-ion battery has attracted more and more attention due to its economic advantage and cycling stability [1–3]. However, low electronic conductivity and low Li^+ ion diffusion rate are still the shortages that limit its application [4,5]. Various studies sought to solve these problems by decreasing the particles size [6,7], doping electronic conductive materials [8–10] and coating carbon [11–13]. Synthesis of $LiFePO_4$/graphene is an effective approach for the surface coating with carbon [14,15].

Some methods were applied to prepare $LiFePO_4$ such as solid-state route [16–18], sol-gel method [19,20], hydrothermal method [21], co-precipitation technique [22] and microwave method [23]. In recent years, many materials have been prepared by a high temperature ball milling method [24–26]. The method is applied to the ball-milling and sintering steps of the synthesis process, and was performed by a patented high-temperature ball mill (as illustrated in Fig. 1). The equipment is modified from a traditional mechanical ball-mill by equipping heating and automatic temperature-controlled elements. The method enables the ball milling and high temperature to bring the energy acting on the reactants at the same time

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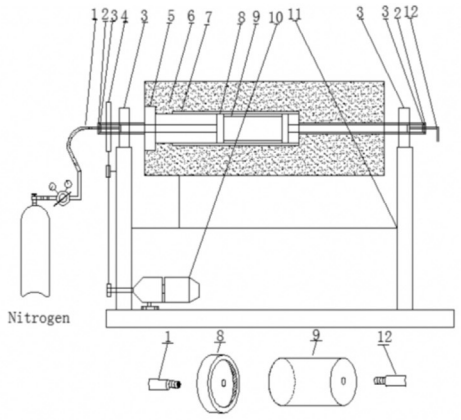

1-nitrogen inlet; 2-sealing ring; 3-bearing; 4-chain wheel; 5-flange; 6-insulation layer; 7-heating elements; 8-sealed copper cap; 9-copper jar; 10-centrifugal machine; 11-stainless stand; 12-gas outlet.

Fig. 1 – Illustration of the high temperature ball mill.

[27,28]. Ultrasonic irradiation transmits acoustic energy into the liquid and brings cavitation and acoustic streaming, which break the large droplets into smaller droplets and the liquid is emulsified. Ultrasound assisted reaction is considered as an effective technique because of its simple operation, easy control, short reaction time and high efficiency [29]. Ultrasound was applied to prepare the precursors of products in this study.

In this work, ultrasound assisted high temperature ball milling method is adopt to synthesize the $LiFePO_4$/graphene ($LiFePO_4$/G) cathode material. Firstly, all the raw materials were added in deionized water, ultrasound can promote the dispersing of the precursor in solution; secondly, precursors were put in a high-temperature ball mill, the milling and roasting of precursors occur at the same time to prepare the product. The structure and electrochemical performances of prepared $LiFePO_4$/G were characterized.

Experimental

Materials synthesis

The raw materials are lithium dihydrogen phosphate (LiH_2PO_4, AR), iron (III) oxide (Fe_2O_3, AR), glucose monohydrate ($C_6H_{12}O_6 \cdot H_2O$, AR) and polyethylene glycol 12000 (PEG 12000, AR). Highly conductive thin graphene layers aqueous slurry (10 wt%, Graphene Nanotechnology Co., China) is used as graphene source. The reaction of prepared $LiFePO_4$ is as represented by Eq. (1):

$$12LiH_2PO_4 + 6Fe_2O_3 + C_6H_{12}O_6 \cdot H_2O \rightarrow 12LiFePO_4 + 6CO\uparrow + 19H_2O\uparrow \quad (1)$$

LiH_2PO_4 (64.229 g) and $C_6H_{12}O_6 \cdot H_2O$ (9.912 g) were weighted and dissolved in distilled water, after which Fe_2O_3 (47.906 g) and thin graphene layers aqueous slurry (18.931 g, product mass carbon content of 2 wt%) were added into the solution, and then maintained ultrasonic irradiation by HC-SH28800 ultrasonic instrument (Create Ultrasonic Technology Co., China) for 1 h. A precursor of $LiFePO_4$/G was obtained after drying at 120 °C for 12 h.

The obtained precursor was poured into a high temperature ball mill, and the weight ratio of precursor and steel balls was 1:12. A ball milling process was firstly reactor temperature at 300 °C ball milling for 1 h, and then the synthesis process temperature maintained at 650 °C ball milling for 8 h in a nitrogen atmosphere to prepare $LiFePO_4$/G. The synthesis process of $LiFePO_4$/G is shown in Fig. 2. This method is a facile and efficient approach to synthesis $LiFePO_4$/G.

As a reference, the $LiFePO_4$/C was also synthesized under the same conditions with $C_6H_{12}O_6 \cdot H_2O$ (22.935 g) and PEG

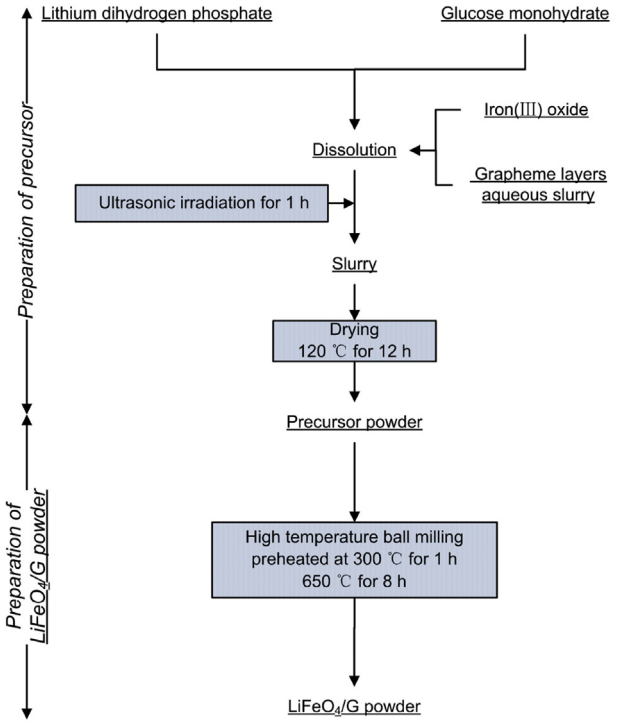

Fig. 2 – Schematic illustration of synthesis processes of $LiFePO_4$/G.

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