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Hydrothermal preparation and performance of $LiFePO_4$ by using Li_3PO_4 recovered from spent cathode scraps as Li source

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ABSTRACT

A novel process recycling Li from the spent $LiFePO_4$ cathode material has been put forward. The new $LiFePO_4$ sample is synthesized through hydrothermal reaction by using recovered Li_3PO_4 as Li source and $FeSO_4{\cdot}7H_2O$ as Fe source. The morphologies, structure and physicochemical properties of the re-synthesized $LiFePO_4$ cathode material were characterized by Field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), Transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS) and electrochemical measurement. The results showed that the morphology and particle size of re-synthesized $LiFePO_4$ samples become more regular and smaller with the increase of the hydrothermal reaction temperature. Besides, it has been found that the $LiFePO_4$ cathode material synthesized at 200 °C showed excellent electrochemical properties which deliver a high initial capacity of 144.25 mAh/g at the rate of 1 C and high capacity retention of 96.7% after 200 cycles. Therefore, this work provides a new strategy for recovery and recycle of the spent $LiFePO_4$ cathode scraps.

1. Introduction

Over the past few decades, the growing concern over fossil fuel consumption and environmental pollution have led to attention for new energy storage system (Whittingham, 2004; Zeng et al., 2014). Lithium-ion batteries have been currently becoming the mainstream of commercial secondary batteries which are considered as the best power source for a sustainable transport system (Chagnes and Pospiech, 2013; Xu et al., 2008). Particularly motivated by the expansion of electric vehicles (EVs), the lithium-ion batteries industry is expected to have a huge development with an global markets expected to be close to $32 billion by 2020 (Palacin and Guibert, 2016; Dunn et al., 2015). As we all know, the battery is the key to the development of electric vehicles (EVs) (He et al., 2009). Considering lithium-ion batteries can provide a high energy density than the previously commercialized batteries, lithium-ion batteries (LIBs) have been considered as the ideal power source which have been applied widely in electric vehicles (EVs) (Tarascon, 2010; Wang and Sun, 2012).

Energy density, power density, cycle life, safety and cost are always the main factors considered as cathode materials of lithium-ion battery for the application of electric vehicles (EVs) (Park et al., 2011). $LiFePO_4$ with the typical olivine structure has been considered as one of the ideal cathode materials due to the low cost, good safety and long cyclic life. As a result, the $LiFePO_4$ batteries have widely been used as large-scale energy storage devices and EVs, especially the power of the public transport, such as bus (Wang et al., 2013). China is the major production and consumption country of $LiFePO_4$ batteries with production amount of $LiFePO_4$ reaching 74,400 ton in 2017 which is account for 65% of the global market. Driven by the rapid development of EVs and HEVs, the market of $LiFePO_4$ batteries is expected to expand continuously with an estimated growth rate of 20% in the period of 2017-2020 (Li et al., 2017).

However, due to the huge usage and growing demand of $LiFePO_4$ batteries, there will be a large number of $LiFePO_4$ batteries facing the disposal or retirement in the near future (Chen et al., 2013; Bian et al., 2016). If these spent $LiFePO_4$ batteries were discarded without recycling, it will lead to a spent of valuable resources and serious environmental pollution (Chen et al., 2016). For example, the $LiPF_6$ in the organic electrolytes will gradually transfer to soil and groundwater (Zeng et al., 2014). What's more, lithium salt is indispensable material in lithium batteries, as the consumption of lithium battery increased quickly year by year, the shortage of lithium resources is getting worse. Taking into account the spent lithium batteries still contain considerable lithium resources, the recycling of lithium resources from spent

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$LiFePO_4$ batteries is highly desirable, so green recycling processes of $LiFePO_4$ batteries have become a research hotspot. Many works have been carried out to recover useful elements from the spent $LiFePO_4$ batteries, lithium is usually recovered in the form of Li_2CO_3 by chemical precipitation reaction (using Na_2CO_3) (Cai et al., 2014; Shin et al., 2015; Zheng et al., 2016). It is mainly because Li_2CO_3 is good lithium source for preparing $LiFePO_4$ through carbothermal reduction process. But the solubility of Li_2CO_3 ($Ksp = 8.15 \times 10^{-4}$) is 1.33 g/100 ml, it indicates that there is still a small amount of lithium remain in the solution during the recycling process. Moreover, although solid-state reactions are commonly thought to be a useful method for preparing $LiFePO_4$, the disadvantages (high energy consumption and uncontrollable grain growth) associated with this method are inevitable (Wang et al., 2012). The solution routes are superior to the solid-state routes in controlling nucleation and crystal growth, and so the morphologies of the products can be fine-tuned easily. Besides, the phase purity, intrinsic defect concentration, grain size, and morphology could be reasonably controlled by solvothermal conditions (Saravanan et al., 2010; Yang et al., 2010; Demazeau, 1999). Considering that lithium is the most valuable element in spent $LiFePO_4$ materials, therefore, it is necessary for exploring a simple method to recover Li element as much as possible.

In this work, a new method is put forward to recycle Li element as Li_3PO_4 from spent cathode scraps and this is the first time that $LiFePO_4$ material synthesised by the recovered Li_3PO_4 and $FeSO_4 \cdot 7H_2O$ as Fe source and P sources through hydrothermal reaction. Taking into account the solubility of Li_3PO_4 (0.038 g/100 ml) at room temperature is far small than Li_2CO_3 (1.33 g/100 ml), therefore based on the technique route of Li_3PO_4 it can ensure to maximize recovery of lithium in the solution. Furthermore, it has been reported that $FeSO_4 \cdot 7H_2O$, H_3PO_4 and $LiOH \cdot H_2O$ were used as starting materials to synthesis $LiFePO_4$ at 180 °C through hydrothermal process (Nan et al., 2013; Jin et al., 2008; Rastgoo-Deylami et al., 2013). In this work the starting materials of re-synthesizing $LiFePO_4$ were the recovered Li_3PO_4 and $FeSO_4 \cdot 7H_2O$. Since the recovered Li_3PO_4 was used as both Li source and P source for synthesising $LiFePO_4$, it can make the whole reaction process become simple and facile. In the same time the element P in the PO_4^{3-} is also availably utilized and avoids the emission of phosphorus containing wastewater. Especially, the $LiFePO_4$ material synthesized at higher reaction temperature of 200 °C shows smaller particle size and better electrochemical performances. The influences of the reaction temperature on the physicochemical and electrochemical properties of $LiFePO_4$ cathode material are systematically studied.

2. Experimental section

2.1. Recovery of Li_3PO_4 from the $LiFePO_4$ scraps

The process sketch for recovery of Li_3PO_4 is showed in Fig. 1. 15 g $LiFePO_4$ scraps pieces were immersed into 0.2 mol/L NaOH solution and stirred mechanically for 0.5 h. After the $LiFePO_4$ cathode material completely removed from the Al foil, the Al foil can be recycled directly after cleaning. Then, the $LiFePO_4/C$ material in the alkaline solution can be separated by filtering. The $LiFePO_4/C$ mixture was dried at 80 °C for 12 h, followed by ball-milling to obtain $LiFePO_4/C$ mixture powders.

$LiFePO_4/C$ mixture powders were calcined at 600 °C to ensure ferrous iron to completely oxidized, because the oxidized material will be more easily dissolved in HCl solution, the precipitation reaction can be represented as

$$12LiFePO_4 + 3O_2 \rightarrow 4Li_3Fe_2(PO_4)_3 + 2Fe_2O_3 \quad (1)$$

Table 1 shows the composition of the mixture after calcination. Then 10 g mixture powders were dissolved in HCl solution (4 mol/L), then 6 mol/L $NH_3 \cdot H_2O$ was used to adjust the pH of solution to 2 and the Fe^{3+} ions will precipitate in the form of $FePO_4$.

After the $FePO_4$ was separated from the solution, 6 mol/L $NH_3 \cdot H_2O$ was added into the filtrate slowly for adjusting filtrate pH to 7, followed by adding a certain amount of Na_3PO_4 into the filtrate to obtain Li_3PO_4. In order to ensure the recovered Li_3PO_4 to meet the requirement of battery-grade, the as-prepared Li_3PO_4 was further dissolved in 2 mol/L H_3PO_4 solution to remove a tiny impurity, followed by adjusting pH value to neutral to purify Li_3PO_4. Then the recovered Li_3PO_4 was washed several times with distilled water and ethanol, and finally dried at 80 °C in air.

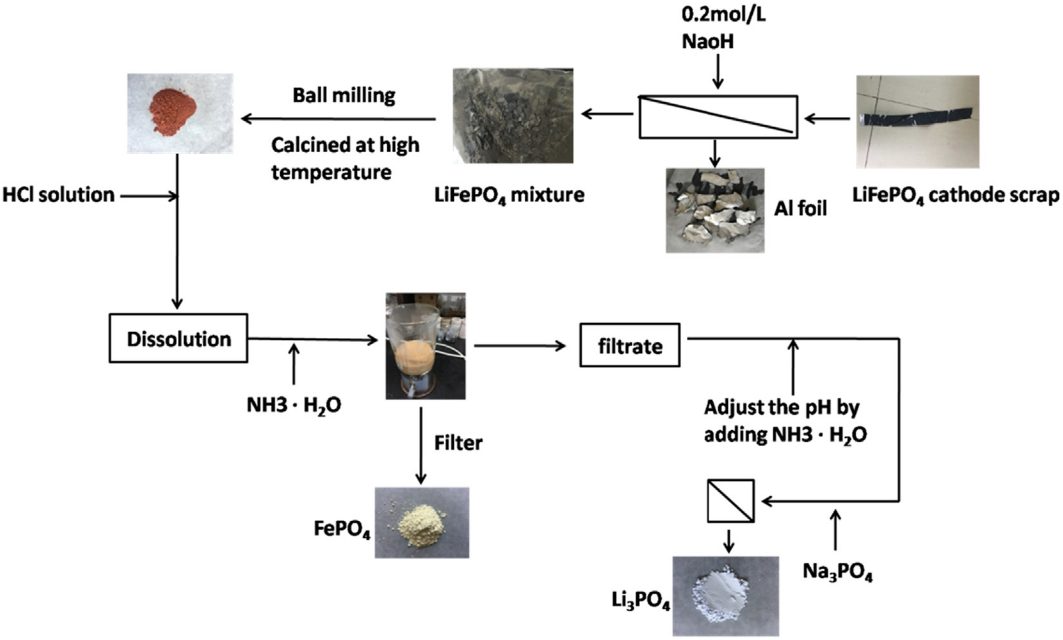

Fig. 1. Process sketch for recycling $LiFePO_4$ cathode scraps.