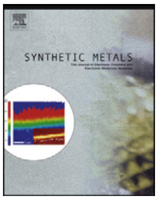
Synthetic Metals 162 (2012) 1315–1326

Contents lists available at SciVerse ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Review

Advances in new cathode material $LiFePO_4$ for lithium-ion batteries

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ARTICLE INFO

Article history:
Received 28 February 2012
Received in revised form 15 April 2012
Accepted 21 April 2012

Keywords:
Lithium-ion batteries
Cathode material
$LiFePO_4$

ABSTRACT

The cathode materials of lithium-ion batteries are developing towards the direction of high energy density, long cycle life, low cost and environment friendly. As a potential 'green' cathode material for lithium-ion power batteries in the 21st century, olivine-type lithium iron phosphate ($LiFePO_4$) become more attractive recently for its high theoretical capacity ($170\,mAh\,g^{-1}$), stable voltage plateau of 3.5 V vs. Li/Li^+, good stability both at room temperature and high temperature, excellent cycling performance, high safety, low raw material cost, no pollution, and rich source of raw materials, etc. This paper introduces the research progress in recent years on the structure and performance, synthesizing methods, carbon-coating, ion-doping and particle size control. Furthermore, the prospect of $LiFePO_4$ cathode material for the lithium-ion batteries is reviewed. (i) Preparation process of $LiFePO_4$ (including high temperature solid-phase method, sol–gel method, microwave method, hydrothermal method, carbothermal reduction method, spray pyrolysis method and other synthesis routes). (ii) Progress on modification of $LiFePO_4$ (three modification strategies including carbon coating, metal particle or ion doping and the optimization of the particle size and morphology). (iii) Finally, the trend of research and development of $LiFePO_4$ is also pointed out (the follow-up studies should be directed at the theoretical study and process improvement).

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0379-6779/$ – see front matter
http://dx.doi.org/10.1016/j.synthmet.2012.04.025

1. Introduction

Since the commercialization of lithium-ion batteries, cathode materials have always been the hot area of research [1–5] because of that determines the energy density, rate capability (i.e., power density), and cost of lithium-ion batteries is the cathode. The major intercalation cathode materials currently being explored are $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and their composites [6–9]. Among the above mentioned cathode materials, $LiCoO_2$ is toxic and very expensive, pure $LiNiO_2$ is iso-structural with $LiCoO_2$ but cannot commercialized solely because of safety concerns after exothermic oxidation of the organic electrolyte with the collapsing delithiated Li_xNiO_2 structure [10], and the cycling and thermal stability of $LiMn_2O_4$ are limiting factors in its application as a cathode material [11,12]. Though $LiCoO_2$ cathode material has been widely used in lithium-ion batteries, the better performance, lower cost and increased safety are expected by the researchers. Since the pioneering study on lithium iron phosphate ($LiFePO_4$) material invented by J. B. Goodenough et al. [13] is a very promising choice of cathode materials for powering electric vehicles (EVs), hybrid electric vehicles (HEVs), electric bicycles and power tools because of its inexpensive, non-toxic, environment friendly and exhibits reversible electrochemical lithium insertion/extraction reactions at ~3.5 V (vs. Li/Li^+) with a theoretical capacity of 170 mAh g^{-1} [14]. In addition, $LiFePO_4$ also has the good cycle stability and the excellent thermal stability. Due to these advantages, $LiFePO_4$ has been attracting much attention as a promising new cathode electrode material for lithium-ion batteries. However, the low intrinsic electronic conductivity of $LiFePO_4$ and the low diffusion coefficient of Li^+ are the main shortcoming that limited its application in industry. Bare $LiFePO_4$ is an insulator with an electrical conductivity of about 10^{-9} to 10^{-11} S cm^{-1}, and the chemical diffusion coefficients were found to be in the range of 10^{-11} to 10^{-13} cm^2 s^{-1} depending on the Li^+ concentration and the characterization method used [10,15]. The poor electrical and ionic conductivity of $LiFePO_4$ causes its small rate capacity and low utilization, and how to overcome these drawbacks has become an important factor of study. Over the past few years, numerous efforts have been devoted to circumvent the drawbacks mentioned above, including coating conductive materials with carbon or fine metal particles [16,17], reducing the particle size and homogeneous particle size distribution [18], tailoring the morphology and texture [19], and selective doping with supervalent cations at lithium site to increase the intrinsic conductivity [20], etc.

A number of comprehensive reviews have discussed the science and technology of $LiFePO_4$ that deal with its structural, synthesis procedures and other electrochemical properties [10,21–27]. Nevertheless, no detailed studies have been conducted to the structure, morphological, synthesis procedures, and modification of $LiFePO_4$ simultaneously. In addition, many new techniques, new processes, new equipments, and new materials were studied recently. Therefore, this paper not only summarized the synthesis method of $LiFePO_4$ including high temperature solid-phase method, sol–gel method, microwave method, hydrothermal method, carbothermal reduction method, spray pyrolysis method and other synthesis routes, but also presented three different approaches to improve the performance of $LiFePO_4$: carbon coating, metal ion or metal oxide coating, ion-doping, optimization of the particle size and morphology, and the relative references were analyzed in detail.

The objective of this work was not to review each of the technologies in depth, but rather to present an overview of past and recent findings as well as an analysis of what the future holds for $LiFePO_4$, which should guide the R&D needed to develop $LiFePO_4$, this will be attractive to their potential users. After short presentation of the structural and synthesis methods, useful information related to improve electrochemical properties of $LiFePO_4$ will be reviewed as follows.

2. The structure and characteristics of $LiFePO_4$

The olivine structure of $LiFePO_4$ was shown in Fig. 1. Its space group is *Pmnb* contains four formula units, and the lattice parameters of *a*, *b* and *c* is 0.6008, 1.0334 and 0.4693 nm, respectively [13]. The cation arrangement in $LiFePO_4$ differs significantly from that in the layered and spinel structures. The Li and Fe are located in octahedral sites and P is located in tetrahedral sites with a distorted hexagonal close-packed framework [28]. A FeO_6 octahedron with two LiO_6 octahedron and a PO_4 tetrahedron are edge shared, there is no continuous network of FeO_6, and the PO_4 tetrahedron in the middle of the octahedral. In such a structure, there is a one-dimensional tunnel formed by the edge shared Li octahedra, where the Li^+ are mobile in this tunnel. And the main obstacle in reaching its theoretical capacity is the low intrinsic electronic conductivity and low ion diffusion rate of Li^+ [29].

3. Synthesis method

In recent years, many research groups have focused their efforts on new synthesis routes for the preparation of $LiFePO_4$ to improve its performance, such as solid-state reaction, sol–gel method, microwave processes, hydrothermal synthesis, carbothermal reduction method, spray pyrolysis technology and so forth.

3.1. Solid-state method

Solid-state synthesis is a conventional method for preparing $LiFePO_4$. This method is simple and easy to industrialization. However, the as-prepared product is non-uniform particles, non-crystalline form, and the synthesis time is long. The lengthy and complex procedures requiring repeated grinding and calcination, which lead to the formation of larger particles with lower electrochemical performance. In general, LiF, Li_2CO_3, $LiOH{\cdot}2H_2O$ and CH_3COOLi were used as the lithium source, $FeC_2O_4{\cdot}2H_2O$, $Fe(CH_3COO_2)_2$ and $FePO_4(H_2O)_2$ were used as the iron source, $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$ were used as the phosphorus source.

The electrochemical performances of $LiFePO_4$ varied depending on its raw material. The $LiFePO_4/C$ was prepared using $FeC_2O_4{\cdot}2H_2O$, $NH_4H_2PO_4$ and $LiOH{\cdot}2H_2O$ as raw materials by solid-state reaction [30], the composite without any impurities and the particle size is approximate 500 nm on average, but some particles had a certain agglomeration. However, the $LiFePO_4/C$ showed more excellent rate performance and better cycling stability than pure $LiFePO_4$. The discharge capacities of the $LiFePO_4/C$ were 163 mAh g^{-1} and 157 mAh g^{-1} at 0.1 C and 1 C, respectively. Dong et al. [31] prepared spherical $LiFePO_4/C$ by solid-state method with $FeC_2O_4{\cdot}2H_2O$, $(NH_4)_2HPO_4$ and LiF as the starting materials at 650 °C. The spherical $LiFePO_4/C$ showed good reversibility, its initial