



Review

Methods of synthesis and performance improvement of lithium iron phosphate for high rate Li-ion batteries: A review

T.V.S.L. Satyavani ^{a,*}, A. Srinivas Kumar ^a, P.S.V. Subba Rao ^b^aNaval Science and Technological Laboratory, Vigyan Nagar, Visakhapatnam 530027, India^bDepartment of Physics, Andhra University, Visakhapatnam 530003, India

ARTICLE INFO

Article history:

Received 26 April 2015

Received in revised form

29 June 2015

Accepted 29 June 2015

Available online 20 August 2015

Keywords:

Li-ion battery

Lithium iron phosphate

Solid state synthesis

Solution based synthesis

Electrochemical performance

ABSTRACT

Lithium ion battery technology has the potential to meet the requirements of high energy density and high power density applications. A continuous search for novel materials is pursued continually to exploit the latent potential of this technology. In this review paper, methods for preparation of Lithium Iron Phosphate are discussed which include solid state and solution based synthesis routes. The methods to improve the electrochemical performance of lithium iron phosphate are presented in detail.

Copyright © 2015, The Authors. Production and hosting by Elsevier B.V. on behalf of Karabuk University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Battery technology is a core technology for all future generation clean energy vehicles such as fuel cell vehicles, electric vehicles and plug-in hybrid vehicles. Augmentation of this superior battery technology is essential for deployment of the same in different applications ranging from hybrid electric vehicles to consumer electronics [1,2]. Improved battery performance depends on the development of materials for various battery components [3–6]. Rechargeable lithium cell technology is promising for the future applications. Here, the lithium exists in its ionic state at the anode and hence the rechargeable lithium battery is called **Lithium Ion Battery**.

2. Li-ion batteries

Many researchers worked in developing the rechargeable lithium battery. They have not been able to overcome the associated safety problems, mainly due to the Li metal dendrites deposition during the charging process [7]. The first lithium battery based on Li/Li⁺/Li_xTiS₂ technology was rapidly withdrawn from the market in the beginning of 1970s due to formation of lithium dendrites which short circuited the cell.

Twenty years later, in 1991 a new generation of lithium batteries, i.e., Li-ion batteries (Li_xC₆/Li⁺/Li_{1-x}CoO₂) were commercialized by Sony Corporation. Presently, Lithium-ion batteries are manufactured in bulk, mostly by Japanese manufacturers [8]. This development in Li-ion technology became possible when the metallic lithium anode was replaced with graphite, which has the ability to reversibly intercalate lithium and has reasonably low potential versus lithium. Charge and discharges are related to a reversible “pumping” of lithium ions from one electrode to another. The layered structure of graphite and its high electronic conductivity are favourable for ensuring high efficiency of ionic–electronic processes in the graphite electrode. To achieve significant improvement in Li-ion battery parameters, the approach is to improve and upgrade the cathode materials. Cathode materials are typically oxides and phosphates of transition metals, which can undergo oxidation to higher valences when lithium is removed [9,10]. Although, oxidation of the transition metal can maintain charge neutrality in the compound, large compositional changes often lead to phase changes. Hence, crystal structures stable over wide ranges of composition must be used. This structural stability is a particular challenge during charging, when most of the lithium is removed from the cathode. During discharge, lithium is inserted into the cathode material and electrons from the anode reduce the transition metal ions in the cathode to a lower valence. Fig. 1 presents the working mechanism of Li-ion batteries.

In the case of lithium ion battery, the battery is constructed in a discharged state [11], where all the lithium ions are contained at the cathode and the graphite anode does not contain any lithium

* Corresponding author. Tel.: +91 891 2586129, fax: +91 891 2559464.

E-mail address: tvslsatyavani@gmail.com (T.V.S.L. Satyavani).

Peer review under responsibility of Karabuk University.

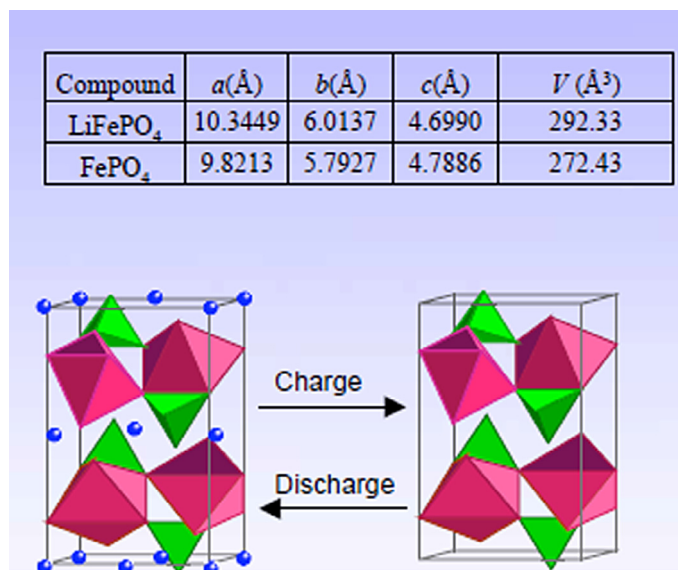
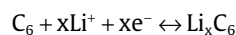


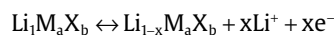
Fig. 1. Working mechanism of Li-ion batteries.

ions. Thus, the batteries need to be charged before use. During the charging process, the oxidation and reduction reactions proceed at the cathode and anode respectively. During the discharge process, these reactions are reversed. Consequently, lithium ion battery reactions proceed by moving only lithium ions and electrons. These battery reactions are very simple when compared to other batteries, where they usually include a reaction of the electrode with the electrolyte. This simple reaction implies that all materials that can release and insert lithium ions reversibly have the potential to become candidates for lithium ion battery electrode materials.

The intercalation process in $\text{Li}_x\text{C}_6/\text{Li}^+/\text{Li}_{1-x}\text{M}_a\text{X}_b$ type cell, at the graphite anode, can be written as:



and analogously at the cathode as:



The effectiveness of the intercalation process is determined by ionic–electronic transport properties of both electrode materials, number of sites available for lithium ions and density of available electronic states around the Fermi level in both electrode materials. Current density of the cell depends on ionic–electronic transport properties in both electrode materials. Consequently, the parameters like cell voltage, capacity, energy density and current density are defined by properties of the cathode and anode materials. The number of charge and discharge cycles and cell life time are significantly conditioned by processes taking place at the electrode/electrolyte interface. Cell safety depends on thermal and chemical stabilities of electrode materials and electrolytes. The rates of these two processes and access of the lithium ions in the electrolyte to the electrode surface control the maximum discharge current.

3. Choice of LiFePO_4

Since the commercialization of lithium-ion batteries, cathode materials have always been an important area of research. The major intercalation oxide based cathode materials currently being explored are LiCoO_2 , LiNiO_2 , LiMn_2O_4 and their composites. Among the

Table 1

Comparison of the properties of different cathodes in 18,650.

| Property | $\text{LiAl}_{0.05}\text{Co}_{0.15}\text{Ni}_{0.8}\text{O}_2$ | LiCoO_2 | LiMn_2O_4 | LiFePO_4 |
|---|---|------------------|---------------------------|-------------------|
| Avg. voltage (V) | 3.65 | 3.84 | 3.86 | 3.22 |
| Theo. capacity (mAh g^{-1}) | 265 | 274 | 117 | 170 |
| True density (g cm^{-3}) | 4.73 | 5.05 | 4.15 | 3.60 |
| Specific energy (Wh kg^{-1}) | 219.8 | 193.3 | 154.3 | 162.9 |
| Energy density (Wh L^{-1}) | 598.9 | 557.8 | 418.6 | 415.0 |
| Materials' cost | 1.628 | 1.824 | 1.159 | 1.219 |
| Energy cost ($\text{Wh US}\$^{-1}$) | 6.08 | 5.05 | 5.97 | 6.31 |

above cathode materials, LiCoO_2 is toxic and very expensive. Pure LiNiO_2 could not be commercialized solely because of safety concerns subsequent to exothermic oxidation of the organic electrolyte with the collapsing de-lithiated Li_xNiO_2 structure. Cycling and thermal stability of LiMn_2O_4 are limiting factors in its application as a cathode material. Properties of different cathode materials are compared in Table 1. Even though LiCoO_2 cathode material is widely used in lithium-ion batteries, researchers demand better performance, lower cost and increased safety.

Another major class is the phosphate based cathode materials in the form of LiMPO_4 ($M = \text{Fe, Co, Ni, Mn}$). It forms olivine structure as can be seen from XRD plots given in Fig. 2. The cathodes LiMnPO_4 , LiCoPO_4 and LiNiPO_4 [12–15] have higher open circuit voltages (4.1 to 4.8 V) than LiFePO_4 (3.5 V) [16] but have lower capacities. Cell voltages and specific capacities change with different metal ion complexes as can be seen from Fig. 3. In addition, $\text{Mn}_2\text{P}_4\text{O}_7$ and $\text{Co}_2\text{P}_4\text{O}_7$ are observed to form in de-lithiated LiMnPO_4 [17] and LiCoPO_4 [15] electrodes respectively. This degrades the life span and can be a safety concern, as oxygen is evolved during the decomposition reaction. Since the pioneering study on lithium iron phosphate (LiFePO_4) by J. B. Goodenough et al. [18], it has become a very promising choice among phosphate based cathode materials. It suits well for powering electric vehicles (EVs), hybrid electric vehicles (HEVs), electric bicycles and power tools because of its low cost, non-toxicity, and environmental benignity. The reversible electrochemical lithium insertion/extraction reactions take place at around 3.5 V (vs. Li/Li^+) with a theoretical capacity of 170 mAh g^{-1} [19]. In addition, LiFePO_4 also has good cycle stability and excellent thermal stability. Due to these advantages, LiFePO_4 is attracting greater attention as a promising new cathode electrode material for lithium-ion batteries.

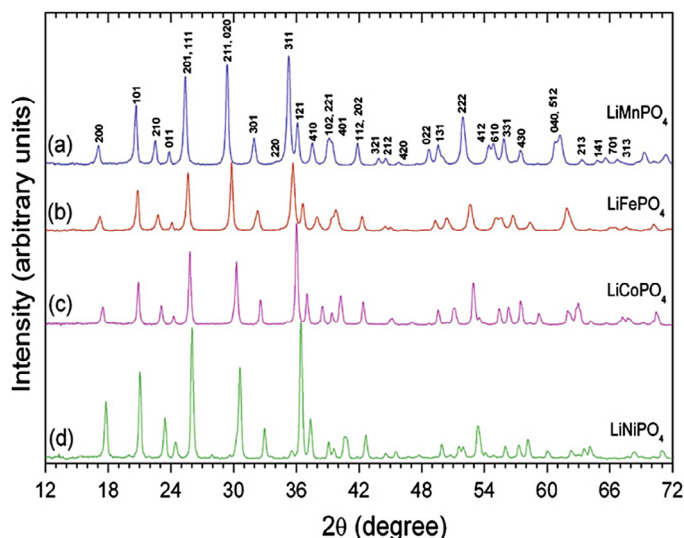


Fig. 2. XRD patterns of LiMPO_4 ($M = \text{Mn, Fe, Co, Ni}$).

Download English Version:

<https://daneshyari.com/en/article/477545>

Download Persian Version:

<https://daneshyari.com/article/477545>

[Daneshyari.com](https://daneshyari.com)