



State of the art and open questions on cathode preparation based on carbon coated lithium iron phosphate



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ARTICLE INFO

Article history:

Received 1 April 2015

Received in revised form

30 July 2015

Accepted 21 August 2015

Available online 1 September 2015

Keywords:

- A. Nano-structures
- B. Electrical properties
- B. Physical properties
- B. Chemical properties
- E. Casting

ABSTRACT

One important component with particular relevance in battery performance is the cathode, being one of the main responsible elements for cell capacity and cycle life.

Carbon coated lithium iron phosphate, C–LiFePO₄, active material is one of the most promising cathode materials for the next generation of large scale lithium ion battery applications and strong research efforts are being devoted to it, due to its excellent characteristics, including high capacity, ~170 mAh/g, and safety.

This review summarizes the main developments on C–LiFePO₄ based cathode film preparation and performance. The effect of the binder, conductive additive, relationship between active material –binder–conductive additive and drying step, in the electrode film fabrication and performance is presented and discussed. Finally, after the presentation of the cell types fabricated with C–LiFePO₄ active material and their performance, some conclusions and guidelines for further investigations are outlined.

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1. Introduction

Modern society increasingly demands efficient energy storage devices for mobile communication applications, computers, electric vehicles and new products such as e-labels, e-packaging, disposable medical testers and drug delivery patches, among others [1,2].

In 2014, the total global market for batteries (both single use and rechargeable) used in portable devices is estimated to be \$ 52.6 billion of dollars [3].

There are different types of batteries, but the ones standing out with respect to use and performance are Lithium-ion batteries (Li-ion) [4].

Lithium-ion batteries are used for Laptops, mobile phones, gift cards, calculators and watches, among others, due to their properties/characteristics such as being lighter, cheaper, showing higher energy density, less charge lost (self-discharge), no memory effect, prolonged service-life, higher number of charge/discharge cycles

in comparison with other battery types, such as Nickel-Cadmium [5–7].

The basic components of a battery are the two metallic collectors, the positive electrode (cathode), negative electrode (anode) and the separator (porous membrane with electrolyte solution), as illustrated in Fig. 1 for a charging and discharging process.

The current collectors are typically metal films placed in each electrode (anode and cathode). Usually, the collector is an aluminum film for the cathode and a copper film for the anode [8]. The main characteristics of the collectors are being good conductors and electrochemically stable within the potential operation window of the electrode [9].

During the charging process (Fig. 1a), electrons and lithium ions (positive ions) move from the cathode to the anode and during the discharge process (Fig. 1b), electrons and positive ions move from the anode to the cathode.

One essential element for the operation of a battery is the separator, as it controls the number of lithium ions and their mobility, serving as medium for the transfer of lithium ions between the electrodes [10–12].

Battery separators are often based on porous polymer membranes, composites and polymers blends, including fluorinated

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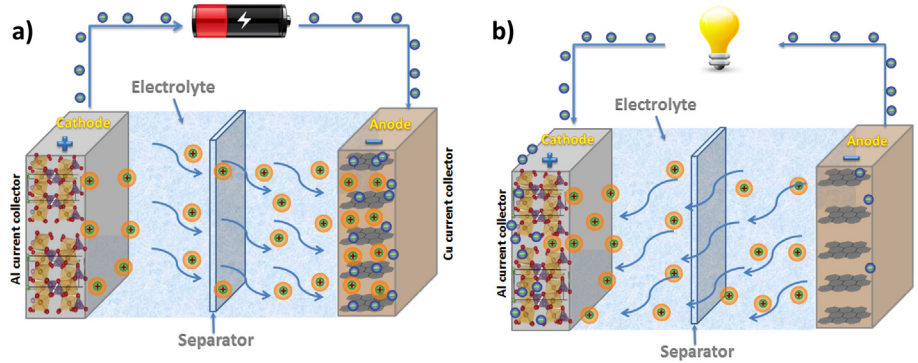


Fig. 1. Representation of the charge (a) and discharge (b) processes of a lithium-ion battery systems.

polymers (poly(vinylidene fluoride) (PVDF) and its copolymers), poly(ethylene oxide) (PEO) and polyolefins [13–17].

The electrolyte solution in which the porous membrane is soaked is typically constituted by salts dissolved in a solvent, water or organic molecules [18].

With respect to the negative electrode (anode), Fig. 1 shows the graphite structure that is among the most used ones for this application [19,20].

Graphite shows a structure formed by a stack of hexagonally bonded sheets of carbon which are held together by van der Waals forces, being able to store lithium ions in a process known as insertion or intercalation [21].

Besides graphite, other carbonaceous materials such as carbon nanotubes (CNT) [22] and graphene [23] are used for anode applications [24].

Carbonaceous materials for the fabrication of battery anode electrodes show the largest potential for improving lithium ion-cells. These electrodes are highly conductive which results in enhanced electronic transport [21] but, on the other hand, suffer from low rate capability and irreversible capacity losses originated by the formation of a solid electrolyte interface (SEI) [25,26].

The positive electrode (cathode) is based on transition metal oxides and phosphates as they show strong ionic character and a densely packed crystal structure [27–29].

The most important characteristics of cathode materials are a high electrochemical reactivity and being light and densely packed to allow high capacity per weight. The cathode active material is responsible for the cell capacity and cycle life [29].

The most used materials for cathode electrodes are lithium transition metal oxides (LiMO_2 , $M = \text{Co, Ni, Mn}$; lithium cobalt oxide (LiCoO_2) [30], lithium manganese dioxide (LiMnO_2) [31], lithium nickel oxide (LiNiO_2) [32]) and lithium transition metal phosphates (LiMPO_4 , $M = \text{Mn, Co, Ni}$ and Fe).

The most promising LiMPO_4 cathode material is lithium iron phosphate (LiFePO_4) [33]. LiFePO_4 is considered the most promising innovative cathode material for the next generation large scale lithium-ion battery applications, including the automotive industry (hybrid electric vehicles (HEVs) and electric vehicles (EVs)), due to its stable chemistry and non-explosive behavior [34,35].

LiFePO_4 shows excellent properties, being the most relevant ones the relatively low cost (due of the presence of iron (Fe) in its composition, which is cheaper and environmentally friendlier than cobalt (Co)), low density (3.6 g/cm^3) in comparison with other materials (LiCoO_2 , 5.1 g/cm^3 ; LiNiO_2 , 4.8 g/cm^3) and a high theoretical capacity of 170 mAh/g ($2.0\text{--}4.0 \text{ V}$) [29,34].

Table 1 shows the most important advantages and disadvantages of LiFePO_4 as active material.

The crystalline structure of LiFePO_4 is the spinel olivine structure with a Pnma space group, as it is illustrated in Fig. 2 for the xy and xz planes [36].

Fig. 2 shows that the O sites form a nearly tetrahedral arrangement around each P site and also an approximately octahedral arrangement around each Fe site [36].

As it is shown in Fig. 2, Li ions are located in the octahedral channels along the y axis, allowing their mobility.

The charging reaction (Fig. 1a) for this cathode material is:



The discharge reaction (Fig. 1b) has the following form:



The charging and discharging processes (delithiation/lithiation mechanism) is divided in two types: diffusion reactions (crystal structure does not change) and phase boundary movement of two-phase reactions, i.e. during the charging progresses, the phase FePO_4 increases and the LiFePO_4 decreases until just the FePO_4 phase remains [29]. In these phases, the unit-cell volume undergoes variations, $\Delta V = 6.5\%$ [41]. The volume change represents an advantage in the design of Li-ion batteries as it compensates for carbon anode expansion. Further, it shows strong structural stability and safety, making it an ideal battery material for electric vehicle applications [29,42].

The largest disadvantage of LiFePO_4 is its low electrical conductivity (10^{-9} Scm^{-1}) [43,44]. In order to overcome this barrier and improve the electrochemical performance and thermal stability of LiFePO_4 it was proposed a carbon coating of the LiFePO_4 nanoparticles with different carbonaceous dopants, as illustrated in Fig. 3 [45,46].

The control of phase purity, particle size and carbon coating of the C- LiFePO_4 composite material improves significantly the electrochemical performance.

Independently of the electrode type, the basic constituents of the electrodes are the active material (such as, C- LiFePO_4), the binder and the conductive additive, altogether forming the electrode film.

The electrode preparation occurs in two steps: first, the different components are mixed in the solvent obtaining the electrode slurry; then, casting, drying and calendaring are performed. The calendaring stage or electrode pressing is an important step, in particular in the industrial production [47,48].

The electrode slurry and film preparation steps are critical in determining the quality of the electrodes in lithium-ion battery systems [48,49].

Taking into account the excellent properties of C- LiFePO_4 , this review focuses on the efforts that have been devoted to the

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