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Review article

LiFePO$_4$/C nanocomposites for lithium-ion batteries

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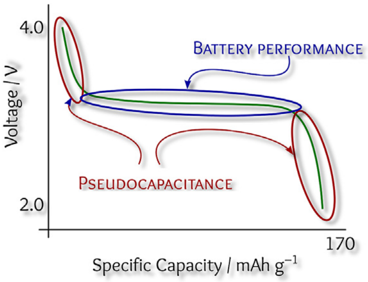
HIGHLIGHTS

- The important of carbon structure in the LiFePO$_4$/C nanocomposites is reviewed.
- It is described that the LiFePO4 lattice is capable of fast charging/discharging.
- The significance of pseudocapacitance in LiFePO$_4$/C electrode is discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

LiFePO$_4$, as the most famous member of the family of olivine-type lithium transition metal phosphates, is one of the promising candidates for the cathodes of lithium-ion batteries. However, its battery performance is limited by its low electrical conductivity and slow Li solid-state diffusion. Various methods have been attempted to improve the battery performance of lithium iron phosphate. Among them, compositing the LiFePO$_4$ with carbon nanomaterials seems to be the most promising, as it is facile and efficient. Carbon nanomaterials usually serve as a conductive agent to improve the electrical conductivity while increasing the material porosity in which the solid-state diffusion distances are significantly shortened. Owing to the popularity of various carbonaceous nanomaterials, there is no straightforward line of research for comparing the LiFePO$_4$/C nanocomposites. This review aims to provide a general perspective based on the research achievements reported in the literature. While surveying the research findings reported in the literature, controversial issues are also discussed. The possible contribution of pseudocapacitance as a result of functionalized carbon or LiFePO$_4$ lattice defects is described, since from a practical perspective, a LiFePO$_4$/C electrode can be considered as a supercapacitor at high C rates (with a specific capacitance as large as 200 F g^{-1}). The Li diffusion in LiFePO$_4$ has not been well understood yet; while the Li diffusion within the LiFePO$_4$ lattice seems to be quite fast, the peculiar interfacial electrochemistry of LiFePO$_4$ slows down the diffusion within the entire electrode by a few orders of magnitude.

1. Introduction

The seminal work of Goodenough and his co-workers revealed the possibility of electrochemical extraction of lithium from LiFePO$_4$ [1]. Since then, considerable attention is paid to the family of olivine LiMPO$_4$ (M is a transition metal) as potential candidates

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for the cathodes of lithium-ion batteries; though, $LiFePO_4$ is still dominantly the most common member of this family. Instead of replacing the current cathode materials in small lithium-ion batteries, the target market of $LiFePO_4$ is large-scale batteries such as electric vehicles and household energy storage because of the low cost and safety.

Various approaches, which are indeed common methods in the realm of lithium-ion batteries, have been utilized to improve the battery performance of $LiFePO_4$. The simplest method for reducing the rate-limiting factor of the Li solid-state diffusion is to reduce the particle size as the diffusion lengths are shortened. The primary disadvantages of this method are a lower tap density as a result of a higher porosity and electrochemical instability due to the large contact area between the electroactive material and electrolyte. The latter can result in harmful interfacial phenomena such as facilitating the transition metal dissolution in the electrolyte. In any case, this approach has become more common by the popularity of nanomaterials. $LiFePO_4$ nanomaterials with small particle sizes have been synthesized via various synthesis routes and investigated as potential cathode materials [2–10].

A key issue in the electrochemistry of $LiFePO_4$ is the possibility of the $LiFePO_4$–$FePO_4$ phase transformation [1,11–24], which is generally believed that might be disappeared for smaller nanoparticles. Nevertheless, Satam et al. have recently shown that the miscibility gap appears even for $LiFePO_4$ nanoparticles as small as 5 nm [25].

Doping is another common approach for stabilizing the lattice structure of this class of inorganic electroactive materials. The electrical conductivity of $LiFePO_4$ can be enhanced by this approach, but the overall improvement in the battery performance is not enough to address the practical requirements. Xu et al. have recently discussed the usefulness of metal doping for improving the battery performance of $LiFePO_4$ [26]

Armand and his co-workers first suggested that adding carbon additives can significantly improve the battery performance of $LiFePO_4$ to achieve a practical, specific capacity close to the theoretical capacity [27]. The critical issue in designing carbon-based $LiFePO_4$ cathode material is that the amount of carbon should be minimized, since adding the high surface area carbon nanomaterials lowers the tap density and consequently the energy density [28]. Furthermore, the nanocomposite architecture should be subtly designed to minimize the porosity while providing enough space for the fast diffusion of Li ions within the electrode. Zhao et al. showed that even microstructure of $LiFePO_4/C$ can have an enormous impact on the battery performance [29]. Of course, such comparative studies cannot be simply interpreted, as the changes in the morphological structure are not merely representative of the physical changes in the particle size and structure since the chemical structure is also altered to some extent. Therefore, it is difficult to precisely find what is responsible for the improvement in the battery performance.

Various carbon nanomaterials such as graphite [30,31], carbon black [30–34], acetylene black [30,31,35], ketjen black [36], nanotubes [30,37–40], *etc.* have been employed for the preparation of $LiFePO_4/C$ nanocomposites. Although the carbon is subject to structural changes during the thermal treatment (and graphitization to some extent), comparative studies have suggested that graphite or graphitic carbon has better performance [30,31]. Depending on the starting carbon nanomaterial, the $LiFePO_4$ particles might be agglomerated [30], which is not in favor of the desirable battery performance. Ordered mesoporous carbon (OMC), for example, is a common carbon nanomaterial for the confinement of electroactive materials for energy storage and conversion [41]. There are reports on embedding the $LiFePO_4$ nanoparticles within the OMC mesopores [42]. This architecture significantly improves the electrical conductivity between the $LiFePO_4$ nanoparticles through the mesoporous network of carbon, and thus, the corresponding electrode can reach a high specific capacity close to the theoretical capacity of $LiFePO_4$, but the rate capability is not good. This is due to the long solid-state diffusion path deep into the mesopores. Therefore, the most common approach is coating the $LiFePO_4$ particles with a thin layer of carbon to preserve the possibility of diffusion into the $LiFePO_4$ particles from three dimensions to minimize the solid-state diffusion impact.

Finding the optimum amount of the carbon additive is not easy, as it depends on various factors such as chemical structure, geometrical shape, and size, mismatch with the $LiFePO_4$ particle, *etc*. There are some comparative studies attempting to find the optimum amount of the carbon additive, but various values have been reported [43–45]. However, even for the same carbon sample, the optimum condition can vary dependent on the electrode thickness [46].

Plate-like morphology of $LiFePO_4/C$ in which the $LiFePO_4$ preferential lattice was along the (010) plane has shown a superior battery performance [47–49]. While the slow performance of the cathode material was comparable with those previously reported in the literature, the fast charge/discharge performance was quite good to deliver a specific capacity of 125 mAh g^{-1} at 10C [47], 126 mAh g^{-1} at 20C [49], or 116.9 mAh g^{-1} at 0.5C under a cold atmosphere of -20 °C [48].

In the surface modification of electroactive materials, the focus is usually on the investigation of the interfaces formed to relate them to the potentially improved battery performance [50–52]. Unfortunately, the focus on $LiFePO_4/C$ has been mostly practical, and less attention has been paid to inspect the exact role of the carbon at the $LiFePO_4/C$ interface. It is evident that the presence of carbon improves the overall electrical conductivity of the electrode; charge transfer resistance is reduced, and no longer can be a rate-determining process. However, less attention has been paid to inspect how the solid-state diffusion of Li within the $LiFePO_4$ lattice is speeded up. On the other hand, the Li solid-state diffusion does not seem to be the sole rate-determining step even in $LiFePO_4/C$ in which the electrical conductivity is not a major problem; because no exceptional battery performance has been reported for small particles in which the diffusion lengths are so short [25,53].

Single-particle studies of a porous $LiFePO_4$ microparticle revealed that 90% of the theoretical capacity can be achieved at a 7C rate where the diffusion coefficient is as high as 2.7×10^{-9} cm^2 s^{-1} [54]. This can be a guiding star in studies of $LiFePO_4/C$. If assuming that the role of carbon is to improve the electrical conductivity of the particle interconnections, then, better battery performance should be unlikely. However, as will be reviewed below, there are noticeable reports in the literature. Hence, other mechanisms should be involved in the battery performance of $LiFePO_4/C$.

Here, the aim is to survey the data reported in the literature to get a better overall picture of available cases. The next step is to identify the missing gaps in our knowledge about the electrochemistry of $LiFePO_4/C$. This is vital for drawing a roadmap for using the works reported in the literature in pursuit of the most promising approaches for the practical development of $LiFePO_4$. Fundamentals of $LiFePO_4$ including its history, structure, Li insertion mechanisms, and lattice alteration by doping have been well reviewed elsewhere [15,23,26,55,56], and thus, the focus will be on the $LiFePO_4/C$ material, which has not been adequately surveyed/addressed before.

2. Controversies in the literature

Despite numerous achievements reported in the literature, it is difficult to properly connect all the findings for a better