



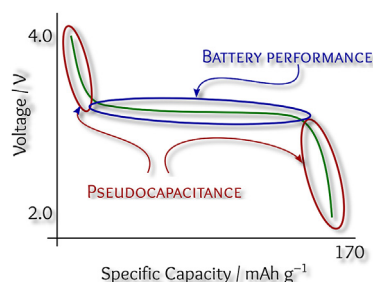
Review article

LiFePO₄/C nanocomposites for lithium-ion batteriesAli Eftekhari ^{a, b, *}^a The Engineering Research Institute, Ulster University, Newtownabbey BT37 0QB, United Kingdom^b School of Chemistry and Chemical Engineering, Queen's University Belfast, Stranmillis Road, Belfast BT9 5AG, United Kingdom

HIGHLIGHTS

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

GRAPHICAL ABSTRACT



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ABSTRACT

LiFePO₄, 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 LiFePO₄ 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 LiFePO₄/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 LiFePO₄ lattice defects is described, since from a practical perspective, a LiFePO₄/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 LiFePO₄ has not been well understood yet; while the Li diffusion within the LiFePO₄ lattice seems to be quite fast, the peculiar interfacial electrochemistry of LiFePO₄ slows down the diffusion within the entire electrode by a few orders of magnitude.

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1. Introduction

The seminal work of Goodenough and his co-workers revealed the possibility of electrochemical extraction of lithium from LiFePO₄ [1]. Since then, considerable attention is paid to the family of olivine LiMPO₄ (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 $2.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ [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

understanding of the LiFePO_4/C system for the commercial development. This review aims to provide a general survey of the data reported in the literature. However, the validity of some data reported in the literature for the practical development of LiFePO_4 cathodes is somehow questionable. In general, there are three types of data, which need to be considered carefully; whether can be extraordinary important or based on a misunderstanding in the data processing.

2.1. Low specific capacity of the original LiFePO_4

The battery performance of LiFePO_4 is poor at high rates or in the course of cycling, but LiFePO_4 is a good electroactive material and can deliver a reasonable electrochemical behavior at low rates. In normal situations, an unmodified LiFePO_4 cathode should be able to deliver a specific capacity over 100 mAh g^{-1} when discharging by a rate at the level of 0.1C. Some approaches show extreme improvements in the battery performance of LiFePO_4 because the original unmodified LiFePO_4 performance is exceptionally poor, e.g., a specific capacity lower than 50 mAh g^{-1} has been reported at 0.1C (see for example [57]). If these works have employed a less electrochemically active LiFePO_4 as the base material, then, applying these approaches to the conventional electrochemically active LiFePO_4 materials should be very practical. In fact, a comprehensive classification is required for the base LiFePO_4 materials.

2.2. Specific capacities higher than the theoretical capacity

There are some papers reporting specific capacities, which are fairly above the theoretical capacity of LiFePO_4 , i.e., 170 mAh g^{-1} (see for example [58,59]). It is controversial if the weight of additives should be considered when calculating the specific capacity or not. The former is of interest for the practical applications as the ultimate goal is to calculate the energy and power density of the whole cell, and the latter for fundamental studies when researchers are interested how much the theoretical capacity of the cathode materials can be achieved during the lithiation and delithiation.

When studying the influence of additives such as carbon coatings or dopants on the battery performance of LiFePO_4 , an excess specific capacity is ambiguous if not profoundly investigated and interpreted. Most likely, the extra capacity is contributed by the other components; then, we still do not know how much of the LiFePO_4 theoretical capacity has been achieved to compare this approach with others. In an unlikely case, the LiFePO_4 lattice has been altered in a way to accommodate a higher amount of Li in comparison with the stoichiometric ratio of the LiFePO_4 chemical composition. Then, it is vitally important to inspect how new rooms have been created for the inserting Li-ions.

Hu et al. reported that the specific capacity of a graphene-modified LiFePO_4 cathode is 208 mAh g^{-1} in which the excess capacity is because of the redox system of 2 wt% graphene [59]. They argued that graphene has a specific capacity of 2000 mAh g^{-1} (assuming each carbon can store one atom of Li) and capable of providing such an enormous excess capacity. Although such a high capacity has not been practically achieved yet, the redox potential is not the same as that of LiFePO_4 . In the corresponding charge/discharge profiles, the excess specific capacity is achieved while the charge and discharge potentials remain intact (the same but longer flat plateau) [59]. The graphene employed in that research seems a conventional sample, but as will be reviewed below, no other paper appeared in the literature is claiming such a high excess capacity because of a graphene contribution. In general, it is neither of fundamental nor practical interest if improving the battery performance of LiFePO_4 without inspecting the exact mechanism of the lithium storage.

2.3. Ultrafast charging/discharging

The rate capability of LiFePO_4 is the most important issue, which should be addressed for commercialization. As mentioned before, for a single-particle electrode in which there is no interconnection of the particles, only 90% of the theoretical capacity can be achieved at the charge/discharge rate of 7C [54]. This can be considered as a best case scenario due to the absence of other limiting factors. Hence, the ultimate goal is to improve the battery performance of LiFePO_4 to reach similar values for a thick electrode. However, there are some unbelievably high rate capabilities reported in the literature. The best example is a paper published by Kang and Ceder claiming to achieve a significant percentage of the LiFePO_4 cathode at an extremely high charge/discharge rate of 400C [60]. This unusual report was criticized by some scientists immediately [61,62]. In any case, no similar result has been appeared in the literature since then. The argument was based on a speculation justifying a fast diffusion along (010) plane of LiFePO_4 to achieve a high diffusion coefficient of $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [63].

LiFePO_4 is known as a cathode material with extremely low diffusion coefficient. However, some works are now suggesting that the solid-state diffusion within the LiFePO_4 is even faster than the fast-charging cathode materials such as LiCoO_2 . If this is the case, the battery performance of LiFePO_4 is limited by complicated and slow interfacial processes between the electrode particles, because such a fast performance has been achieved for a single-particle electrode [54]. Therefore, it is unlikely to achieve a high rate capability for a compact electrode, which is composed of irregular interfaces between the particles.

A critically important point is that the Li de-intercalation/intercalation within the LiFePO_4 lattice is not a linear and straightforward process during the charging/discharging. Fig. 1 depicts how the changes of the Fe valance is non-linear with respect to the charging/discharging stage and how the crystal structure is subject to severe changes in the course of charging/discharging. Therefore, the high-rate performance of LiFePO_4/C is not as simple as considering that a certain percentage of the theoretical capacity has been achieved.

2.4. Unreliable diffusion coefficients

The diffusion coefficient of the electroactive species within the electrolyte solution towards the electrode surface can be measured by common electrochemical equations. However, these equations have been derived by solving complicated fluid mechanic equations only at certain conditions under given assumptions. For instance, the diffusion should be one-dimensional towards the electrode surface. It has been proposed that such equations can be applied to solid-state diffusion for uniform bulk solids such as some glass materials in which the diffusion can be assumed one-dimensional into the glass towards the current collector. However, this assumption is not valid for the solid-state diffusion within the electrode materials of lithium batteries whatsoever [64–68], in which the diffusion is totally three-dimensional from the surface of the material particle towards their centers [69,70]. Fig. 2 compares how the fundamental assumption of the one-dimensional diffusion changes depending on the electrode structure. In lieu of the diffusion from the electrolyte towards the electrode surface in the direction towards the current collector, some Li-ions are diffusing within the porous material in the opposite direction away from the current collector (Fig. 2c). In fact, there is no linear diffusion layer, which is the basis of all these electrochemical equations. Instead, the (imaginary) non-linear diffusion layer is spread three-dimensionally across the neighboring particles (i.e., scientifically meaningless) In practice, the electrode architecture is much more

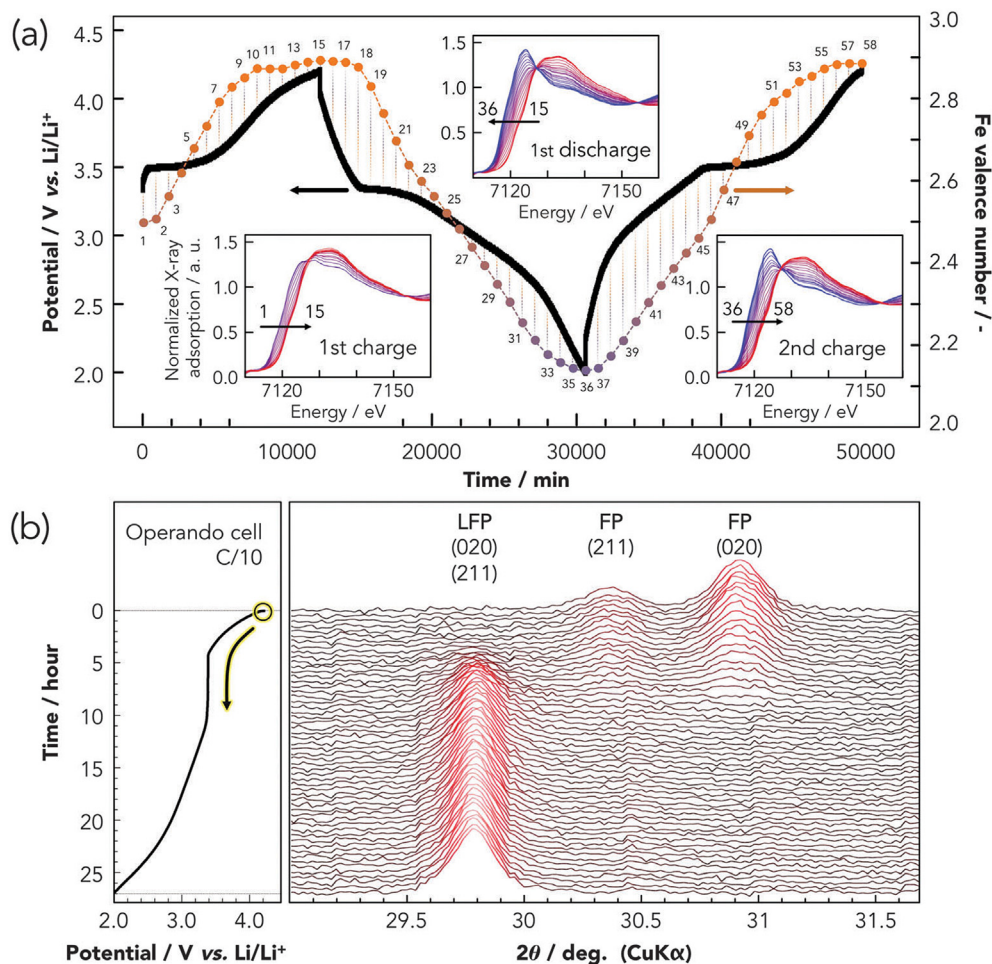


Fig. 1. *In situ* XAFS and XRD measurements on a half-cell consisting of Li/1 M LiPF₆ EC:DEC (LFP/graphitic carbon) composites. (a) The solid bold line shows the galvanostatic charge profile of LFP/graphitic carbon during the *in situ* XANES measurements at 0.1C. Dashed lines correspond to the changes in the evaluated “formal valence number” of Fe during the lithiation–delithiation process. The formal valence number of Fe for the composites was calculated by fitting using commercial LiFePO₄ powder and FePO₄ powder oxidized using the chemical method. The XANES spectra at the iron K-edge of Li_xFePO₄ rate are shown in three insets. (b) Detailed XRD patterns during the second discharge reactions for the 0.1C rate. The voltage profiles during the measurements are shown on the left. Reproduced with permission from Ref. [87]. Copyright 2016, Royal Society of Chemistry.

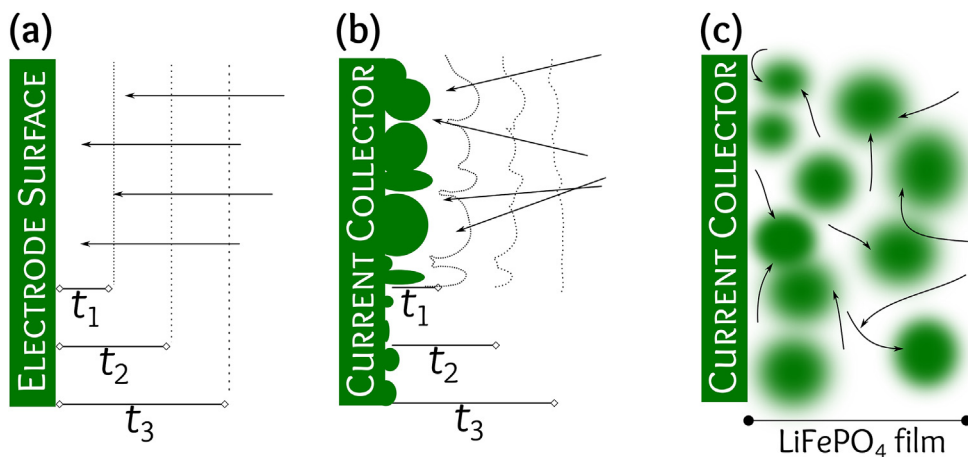


Fig. 2. Schematic illustrations of the diffusion of electroactive species towards or within (a) an ideal electrode, (b) a rough electrode, and (c) a LiFePO₄ film electrode. The boundaries show the growth of the diffusion layer thickness by time. In the case of the rough electrode, the shape of the diffusion layer is no longer flat, and it is too complicated to be drawn within the electroactive film.

complicated as the particles are not of similar sizes and shapes, and the particles are not uniformly packed. One-directional is just a

typical assumption which is invalid for the studies of the electrode materials of lithium batteries, and the invalidity of such equations

have been recently pointed out in the literature [65–68], but such mistakes are still common.

Since the slow solid-state diffusion of LiFePO_4 is a key issue for the practical development of LiFePO_4 , numerous papers have wrongfully employed such equations to calculate the solid-state diffusion coefficient of Li within the LiFePO_4 cathode (see for example [30,71–81]). Owing to the invalidity of these equations, the values reported for the diffusion coefficient do not have a scientific meaning, and thus, should not be used for interpreting the system under consideration. The main issue is that unrealistic values in the range of $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ have been reported for the diffusion coefficient of Li within the LiFePO_4 lattice. Up to now, there is no convincing model or evidence predicting the possibility of such a fast solid-state diffusion within the LiFePO_4 lattice. Furthermore, LiFePO_4 charging/discharging undergoes a possible phase transformation, and thus, the diffusion coefficient is neither linear nor straightforward.

3. Core/shell architecture

The simplest method for the preparation of the LiFePO_4/C core/shell is to form a uniform layer of a polymer on the surface of LiFePO_4 , then, transforming the polymer into carbon [9,10,82–91]. The key advantage of this method is that the LiFePO_4 can be well crystallized before the carbon coating process. In this method, the carbon thickness can be directly controlled by the polymerization process.

This method is not limited to *in situ* polymerization on the LiFePO_4 surface, as various organic compounds can form a uniform layer on the LiFePO_4 particles, which can be easily transformed into carbon by a thermal treatment [92].

Since the crystal orientation plays a critical role in the Li diffusion within the LiFePO_4 lattice, the arrangement of particles controls the accessibility of appropriate channels for fast diffusion through the lattice. This is, of course, a general concept in the structure of such electrodes, but it is of particular importance when the individual particles are coated with a layer of carbon which is not uniform. Therefore, if the Li diffusion is facilitated through the carbon layer at the right position of the lattice structure, a fast charging/discharging process can be expected. Fig. 3 compares the crystal orientations of a series of LiFePO_4/C by high-resolution transmission microscopy (HRTEM).

4. In situ synthesis of LiFePO_4/C

The conventional method for the synthesis of LiFePO_4 is the solid-state reaction of lithium, iron, and phosphate precursors. This process should be conducted under an inert atmosphere to avoid the oxidation of iron. The carbon feedstock can be added to the precursors or using a carbon-based precursor for other components, e.g., using iron citrate as both iron and carbon precursors [93]. Since the synthesis is based on a thermal treatment at a high temperature under an inert atmosphere, the organic compounds will be fully transformed to carbon. Thermal treatment also increases the ratio of graphitic to amorphous carbon.

As alternatives, low-temperature methods such as hydrothermal, sol-gel, co-precipitation, milling, etc. have recently attracted considerable attention, particularly because these methods are capable of forming nanomaterials. An interesting feature of these methods is that the carbon feedstock can be somehow incorporated into the synthesis route. Mechanical synthesis by high energy milling can be utilized for *in situ* preparation of LiFePO_4/C [94,95]. Fig. 4 illustrates how the carbon-coated LiFePO_4 is formed by mechanical milling.

Co-precipitation method usually aims the preparation of iron

phosphate, which will be lithiated at a high temperature in the presence of a carbon feedstock (e.g., glucose) [96]. However, in a sol-gel method, both the LiFePO_4 and carbon are synthesized simultaneously as all precursors are used to prepare the final sol-gel for the essential thermal treatment [97].

One of the key advantages of LiFePO_4 is its low cost in comparison with most potential candidates for the cathode materials. Nevertheless, there is still a growing interest for synthesizing LiFePO_4 from waste sources to make it more economical for the large-scale lithium batteries. For instance, LiFePO_4 can be synthesized from Fe-P slag [98]. Li et al. showed that the role of a carbon source is critical in this process, and the LiFePO_4 lattice structure is dependent on the amount of glucose employed in the chemical reaction, which also results in the formation of carbon too. This suggests that the synthesis of LiFePO_4/C from a waste source is easier than the synthesis of pure LiFePO_4 .

Hydrothermal is another common low-temperature technique for the synthesis of nanomaterials, which has also been successfully employed for the preparation of LiFePO_4/C [47,75,99–115]. The battery performance of the resulting material is strongly dependent on the controllable parameters such as temperature because these factors directly control the size and distribution of the nanocomposite components. Zaghbi and his co-workers showed that stirring has an enormous impact on the battery performance of the LiFePO_4/C material synthesized hydrothermally [99]. Fig. 5 illustrates that the solution pH can result in the formation of entirely different crystal structures, in which the Li diffusion would be different.

In general, several factors affecting the carbon formation are responsible for the battery performance. Thus, there are different reports in the literature for similar materials. For instance, several comparative studies showed that the source of carbon has a strong impact on the LiFePO_4/C performance [116]. Unfortunately, as the thin layer of carbon coated on the LiFePO_4 particles is not inspected separately, there is no solid evidence that how the carbon source is controlling the carbon layer: chemical composition, lattice structure, degree of graphitization, permeability, etc.

5. Carbon coating

One of the common approaches for utilizing a carbon conductive agent is to uniformly cover the LiFePO_4 particles by a uniform layer of carbon. In this case, the electroactive material is not in direct contact with the electrolyte. This can be helpful in forming a more stable solid electrolyte interphase (SEI). On the other hand, the carbon coating prevents the electroactive material from participating in a chemical reaction with the atmosphere [117].

Chang et al. demonstrated by experimental and computational investigations that the intimate contact between the LiFePO_4 and the carbon coating at their interface is of particular importance for better battery performance [118].

The key issue in the core/shell architecture of LiFePO_4/C is the necessity for a uniform coverage of the carbon over the LiFePO_4 particles. On the other hand, the carbon shell stability is of utmost importance, because the long-term cyclability of the cathode is a vital requirement. However, microscopic studies have shown that the LiFePO_4 particles tend to crack in the course of cycling [119]. This is obviously accompanied by breaking the carbon shell too.

It is also possible to conduct the LiFePO_4 crystallization after coating with a carbon shell. In general, thermal treatment is an essential step when preparing the LiFePO_4 in a synchronized process, as the LiFePO_4 crystallization is vital for straightforward battery performance [120]. The primary issue is that there is a serious limitation for the thermal treatment due to the presence of carbon in the material structure. Thus, it is of utmost important to find the

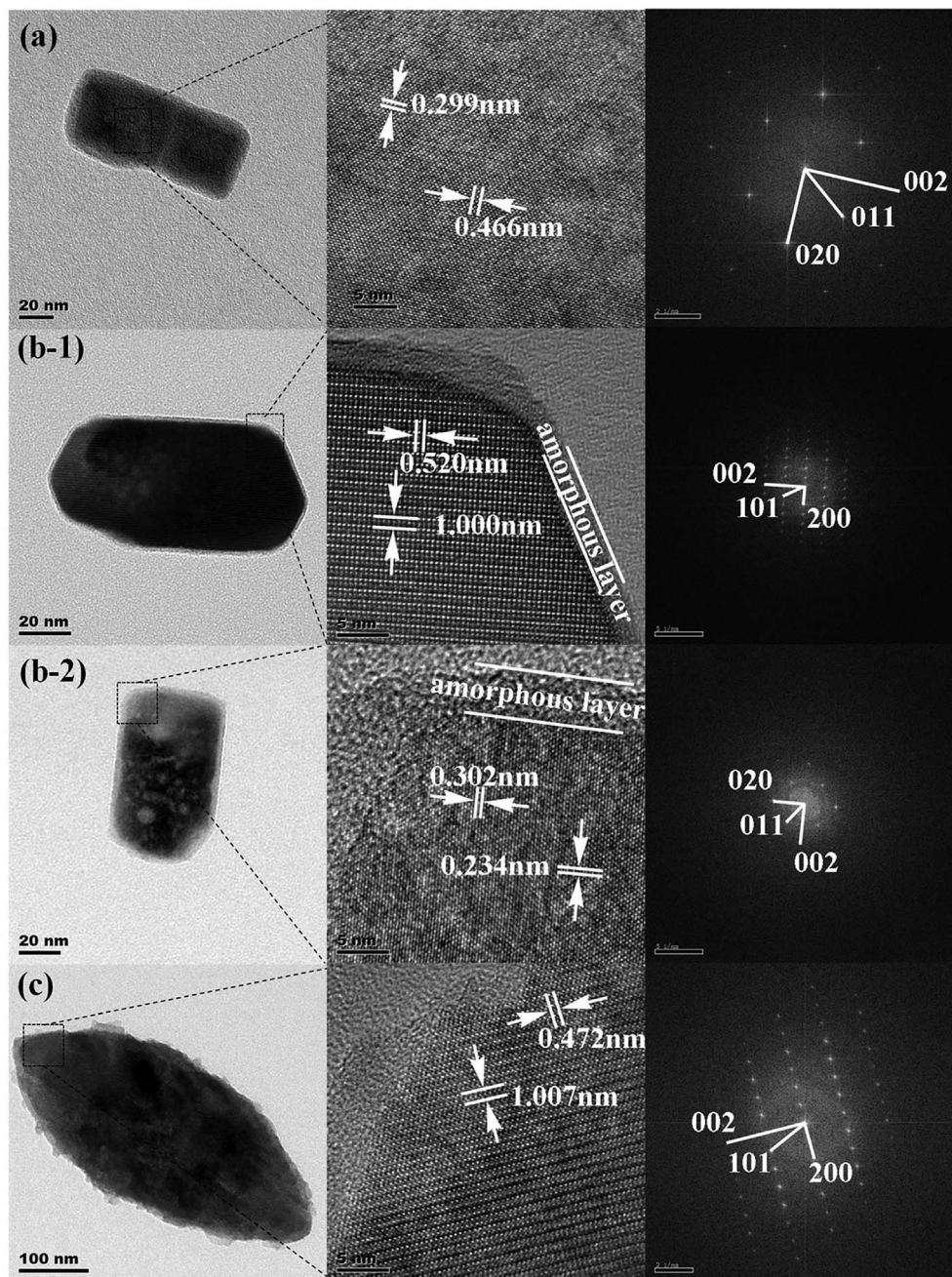


Fig. 3. TEM (left), HRTEM (middle) and their corresponding FFT (right) images of (b-1) long hexagon shape showing the exposed (010) face, (b-2) rectangular shape shows the exposed (100) face; (c) S5, spindle plates show the predominant face (010). Reproduced with permission from Ref. [3]. Copyright 2014, Royal Society of Chemistry.

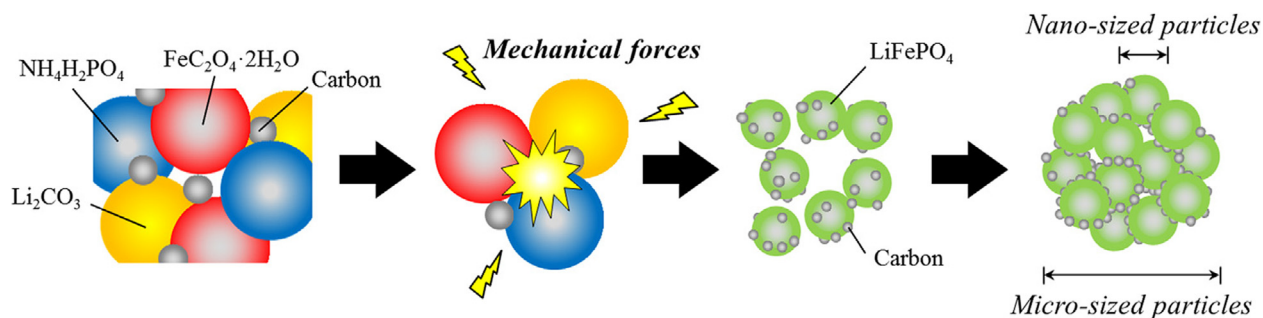


Fig. 4. Schematic illustration of the formation of LiFePO₄/C composite granule. Reproduced with permission from Ref. [94]. Copyright 2014, Elsevier.

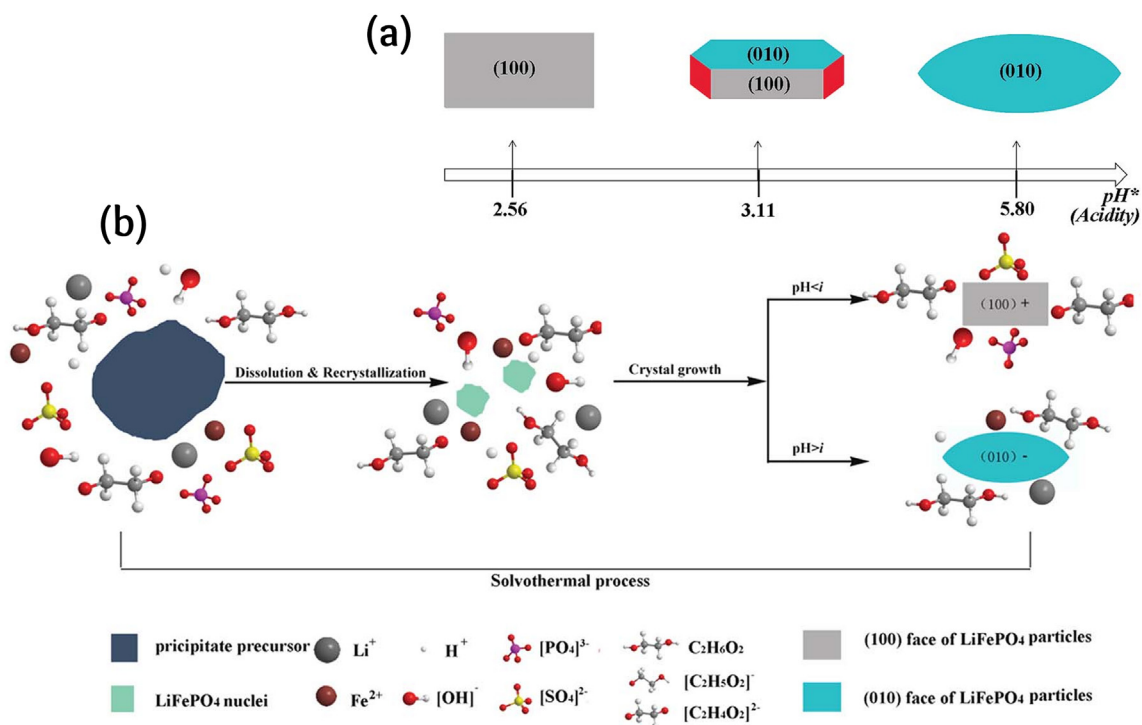


Fig. 5. (a) The particle morphology evolution with the acidity (pH) of solvothermal synthesis environment. Rectangular nanoplates with main exposed (100) face transfer to spindle plates predominantly exposed (010) face gradually as pH of mother solutions increases from 2.56 to 5.80. (b) Schematic illustration of pH influences on LiFePO₄ solvothermal process. *i* is the isoelectric point which refers to a certain pH value during the solvothermal process. When the solution pH < *i*, the net residual electric charge on the surface of the LiFePO₄ particles is expected to be positive, and faces attract different kinds of OH⁻, SO₄²⁻, HO-CH₂-CH₂-O or O-CH₂-CH₂-O negative ions and complexes; when pH > *i*, the particle surface is negatively charged. Particle surfaces will be capped by EG molecules and cations. Reproduced with permission from Ref. [3]. Copyright 2014, Royal Society of Chemistry.

right temperature to adequately conducted the LiFePO₄ crystallization while the LiFePO₄/C interface or the carbon structure is not deformed. The crystallization starts at quite low temperatures (*ca.* 400 °C) but the carbon coating slows it down up to 700 °C, though the uniform shell starts to break at higher temperatures [121]. However, an appropriate thermal treatment can reduce the mismatch at the LiFePO₄/C interface to facilitate the Li diffusion and increase the electrical conductivity (Fig. 6).

In addition to the structure of the carbon coating, its chemical composition also has a significant effect on both the electrical contact and facilitation of the Li diffusion. Doping is the simplest way to tune the chemical reactivity of carbon, and nitrogen is the closest neighbor of carbon in the periodic table to do the job [122–125]. The popularity of nitrogen-doped carbon (mainly graphitic carbons) has been comparable with that of carbon for chemical reaction during the past few years. Covering the LiFePO₄ with N-doped carbon can result in a close-to-ideal performance with a perfectly flat plateau and a specific capacity of over 160 mAh g⁻¹ at 0.1C [123,125]. Similar results have been reported for the LiFePO₄ coated by S-doped carbon [124].

Feng and Wang reported that doping the carbon coating with boron can improve the battery performance to reach 96.5% of the theoretical capacity of LiFePO₄ at 0.1C, while the charge transfer resistance has been significantly reduced [126]. They identified 0.4% as the optimum ratio, as the battery performance is weakening for a higher percentage of the B dopant.

Other materials have also been added to the carbon coating to improve the electrochemical mediation between the LiFePO₄ and the electrolyte [127]. In almost all cases, the battery performance is improved, but since these are electrochemically active materials, it is difficult to profoundly inspect the reason behind an extra

improvement. As a matter of fact, these electroactive materials can contribute to the overall specific capacity one way or another; unfortunately, this issue has not been well studied in the literature.

There are various factors controlling the nanocomposite architecture. Ren et al. compared various carbon nanomaterials providing soft- and hard-contacts with the LiFePO₄ particles and concluded that the so-called soft-contact results in better battery performance [128]. Furthermore, the source of carbon has a considerable impact on the battery performance of the carbon-coated LiFePO₄, and this influence is much stronger at lower temperatures where the role of the carbon is more important [81,85,95,116,129–158].

The formation of the carbon coating is highly dependent on the coating conditions. In a comparison of the carbon coatings prepared by high energy and conventional ball mills, it has been reported that the battery performance of LiFePO₄/C is improved about 20% for the high energy milling [159]. Fig. 4 depicts how ball milling can result in the formation of uniform LiFePO₄/C samples. It should be emphasized that the carbon formed by the high energy mill was more of graphitic nature. Thus, it is difficult to judge if the improvement is due to the better electrical conductivity of the graphitic carbon or a better matching at the carbon/LiFePO₄ interface.

Bai et al. showed that making a 3D nanocomposite by LiFePO₄ and carbon nanowires not only improves the specific capacity but also the electrochemical behavior is significantly improved to display a more well-defined redox system [160]. The role of the carbon agents is not only improving the electrical conductivity but also to provide new channels for the Li diffusion. This is the reason that there is a recent growing interest in using different types of carbon, as the structural mismatch between different geometrical

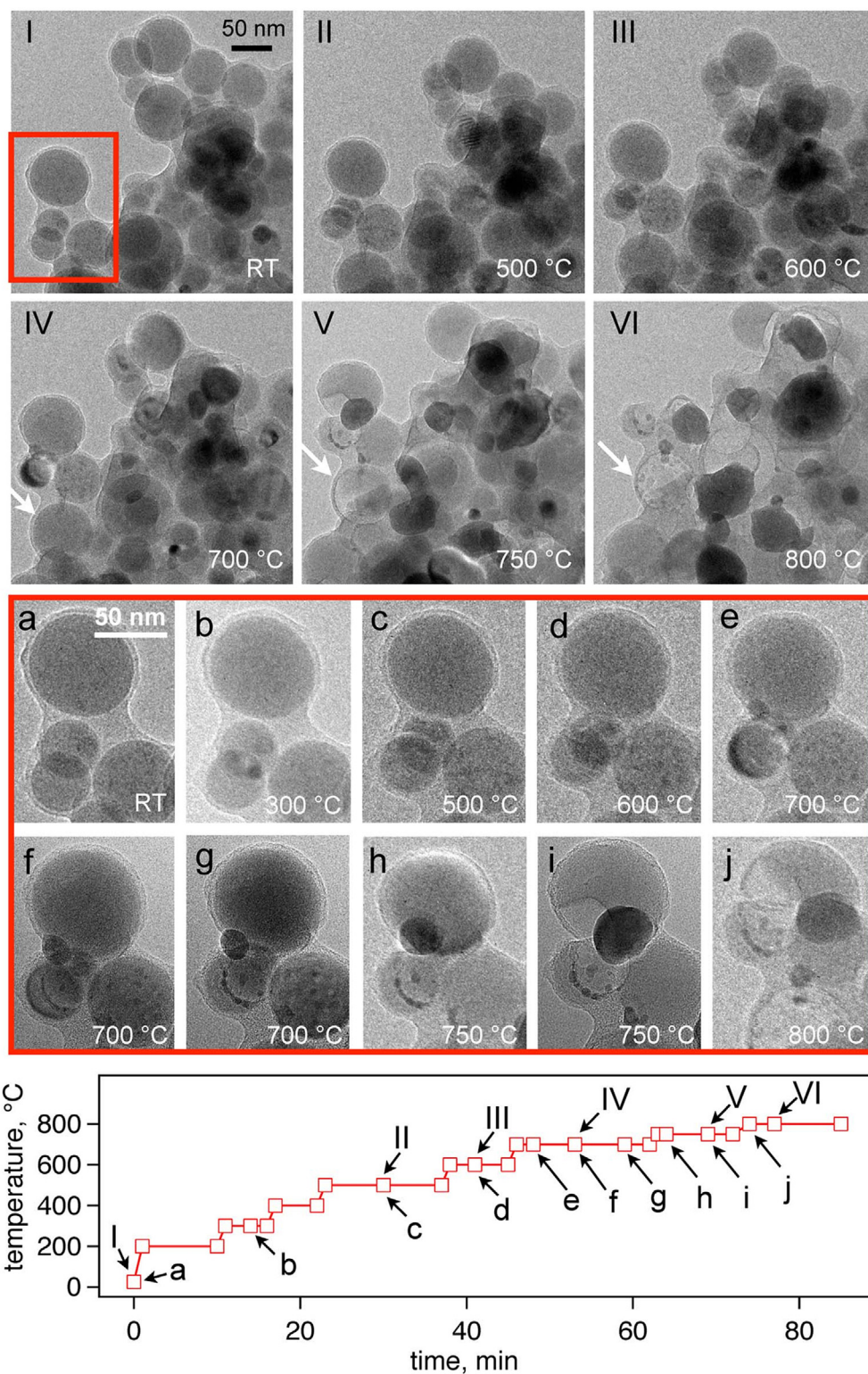


Fig. 6. TEM images of the same area of carbon-coated LiFePO_4 at room temperature (I and a) and different stages of the in-situ heating experiment (II–VI and b–j). The red frame marks an area shown as close-up below. Most changes - in particular the formation of empty carbon shells (an example is marked by arrows) and the particle growth - only occur at temperatures above 700 °C (V, VI and i, j). Reproduced with permission from Ref. [121]. Copyright 2016, Elsevier. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shapes can leave more spacious places within the nanocomposite [161–173].

Winter and his co-workers inspected the impact of the carbon

particle size on the battery performance of $\text{Li FePO}_4/\text{C}$ nanocomposites [174]. They concluded that the overall conductivity is increased by increasing the carbon surface area due to better

distribution over the matrix of the LiFePO_4 particles. This is also because smaller carbon particles can build more contact points with the LiFePO_4 to participate in the electron transport process. However, there is a limit in reducing the carbon particle sizes due to the natural tendency for agglomeration of ultra small particles.

This is not limited to the carbon or the whole nanocomposite structure only but also the entire electrode structure. The porosity of the final electrode should be optimized for facile transport of the Li-ions. In this regard, even the choice of binder can significantly control the battery performance of the LiFePO_4/C [175–180]. Seid et al. demonstrated that the interaction of the carbon coating and the binder has a noticeable impact on the hopping mechanism of the charge transfer [181].

Obviously, an excess porosity is not in favor of the practical applications due to a lower tap density. Furthermore, the existence of porous gaps between the electroactive particles can increase the electron transport distance, which might be a severe issue at high charging/discharging rates [97].

6. The LiFePO_4/C interface

Owing to the high charge transfer resistance associated with low electrical conductivity and slow Li-ion mobility at the LiFePO_4 /electrolyte interface, Gaberscek demonstrated that for fairly small particles, in which the diffusion lengths are not so long, the rate-determining step is the interfacial process for a LiFePO_4 cathode [182]. This suggests that an additional responsibility of the carbon coating is to improve the electrode/electrolyte interface to eliminate slow interfacial processes. Almost all reports (if not all) on LiFePO_4/C show that the charge transfer resistance is reduced as a result of the carbon conductive agent. This behavior is due to the electrode overall conductivity and does not necessarily mean a well-defined electrode/electrolyte interface. To achieve the latter, there is a growing interest in core/shell architecture in which an ultra-thin layer of carbon (ca. 2 nm) is uniformly formed on the LiFePO_4 particles.

Pan et al. compared the LiFePO_4 particles having different interfacial structures, and concluded that the type of bonding between the carbon and electroactive material has a substantial impact on the electrochemical behavior of the system under consideration [183].

7. Graphene

Owing to the popularity, electrical conductivity, and the presence of functional groups, graphene is one of the common forms of carbon for improving the battery performance of LiFePO_4 [28,43,45,46,49,58,59,72,76,91,105,161,162,168,171,184–223]. The content of graphene in the LiFePO_4 /graphene can directly improve the electrochemical behavior as the redox system is strengthened with a lower peak-to-peak separation (up to 5 wt% graphene) [59]. The latter indicates that a smaller overpotential is required for the Li intercalation/de-intercalation; however, this influence is stronger on the de-intercalation process.

In general, the sp^2 carbon can better improve the battery performance in comparison with the sp^3 carbon in a disordered form [192]. This is of utmost importance because the experimental results have shown that the acetylene black, which is used for casting the electrode material, produces a large amount of distorted carbon at the interface. Madec et al. showed that the formation of sp^3 carbon can block the Li intercalation kinetics [224].

In situ synthesis of LiFePO_4 and graphene simultaneously can assist a better connection of the nanocomposite components at the lattice scale [203]. However, thermal treatment seems to be a necessary step to crystallize the LiFePO_4 . There is a prospect for the

in situ formation of LiFePO_4 /graphene nanocomposite by employing graphene oxide as the graphene source [184]. This approach is based on the possibility of the reduction of graphene oxide by Li_2CO_3 or similar materials, which can be used as the lithium source. The flexibility of this approach is that graphene oxide can be tuned by functionalization. The corresponding functional groups can control the LiFePO_4 growth.

8. Capacitive and pseudocapacitive behavior

One important issue, which is usually ignored in the literature, is that increasing the electrode surface area results in a stronger capacitive behavior. Since the double layer is very thin, it fairly forms over the particles throughout the compact electrode. The double layer capacitance is reasonably ignored in common battery studies, as it is negligible at slow rates, however, when charging/discharging a cathode at high rates (*i.e.*, common in the works focusing on the improvement of the LiFePO_4/C battery performance), the double layer capacitance contribution is considerable. However, since most of the carbon nanomaterials (*e.g.*, graphene) are electrochemically activity due to the presence of functional groups, the pseudocapacitance contribution is much more significant [87]. Fig. 7 displays that adding graphene to LiFePO_4 causes a severe deviation from battery performance to pseudocapacitive behavior. Thermal treatment will weaken the pseudocapacitance as the redox systems of functional groups disappear and the electroactive material is crystallized to have a more unified redox sites.

The key difference between the battery performance and pseudocapacitive behavior is that in the former, all redox sites have the same energies and the electrochemical reaction occurs at a narrow range of potential close to the system redox potential, while the latter is based on a series of different redox systems with various energies. As a result, the battery performance is characterized by a flat plateau in the charge/discharge profile as the potential remains constant throughout the entire reaction (Fig. 8a), but pseudocapacitance occurs at a wide range of potentials. In the case of LiFePO_4/C , the potential remains about 3.45 V vs. Li/Li throughout the Li extraction or insertion, but various redox reactions at different potentials occur due to the electrochemical reactions of the functional groups on the graphene.

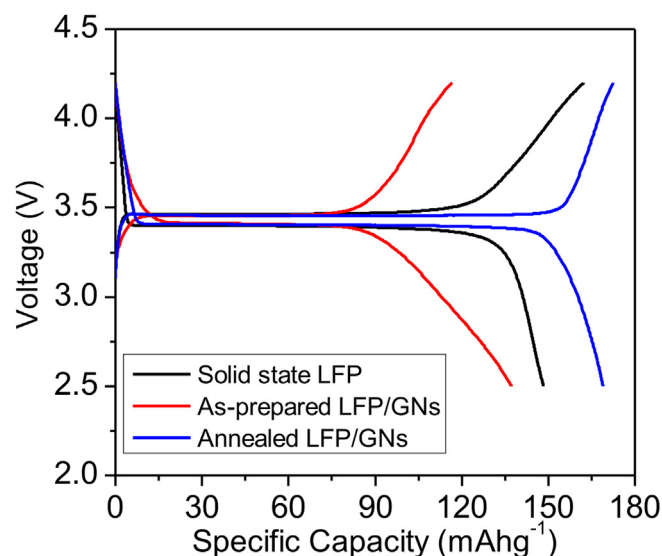


Fig. 7. Charge/discharge profiles of various LiFePO_4 electrodes recorded at 0.5C. Reproduced with permission from Ref. [206]. Copyright 2016, Elsevier.

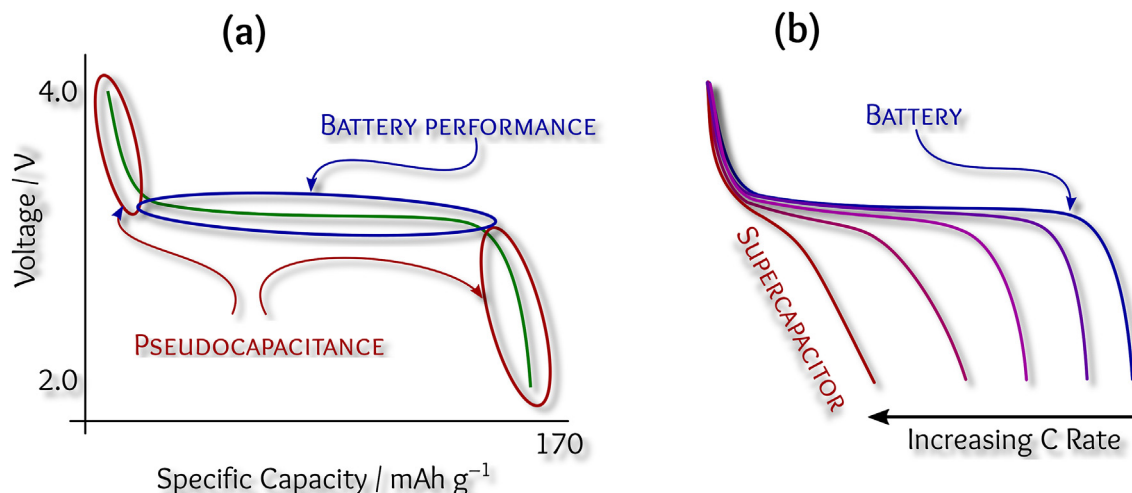


Fig. 8. (a) Typical charge/discharge profile of a LiFePO_4/C electrode at a low C rate (e.g., 0.1C). (b) Transformation of the battery performance of LiFePO_4/C cathode towards a supercapacitor by increasing the charge/discharge rate.

The electrochemical redox of the LiFePO_4 can be extended to a wider potential range if altering the uniformity of the redox sites, e.g., by doping. Kisu et al. subtly demonstrated that the presence of Fe^{3+} defects in the LiFePO_4 structure results in a considerable contribution of the system pseudocapacitance, which occurs at a wide range of potential, even far from the LiFePO_4 redox potential [225]. As a matter of fact, LiFePO_4/C has also been tested as an electroactive material for the fabrication of pseudocapacitors [226–228]. As typically shown in Fig. 8b, the battery performance of LiFePO_4/C tends to transform into a supercapacitor. Roughly speaking, this supercapacitor can deliver a specific capacitive over 200 F g^{-1} , which is fairly comparable with available supercapacitors.

The experimental data presented in Fig. 1 reveals characteristic differences between the battery performance and pseudocapacitance. During the (so-called ideal) battery performance, the Fe valance is dramatically subject to change, but the changes are slight when the electrode delivers a pseudocapacitive behavior. Furthermore, no structural change occurs during the pseudocapacitance.

9. Double coating: the role of an ionic conducting agent

Facilitating the electrical conductivity between the LiFePO_4 particles by gold can improve the battery performance just at high temperature where the diffusion is fast enough [229]. This indicates that the only interfacial rate-limiting process is not the electron transport but also the ion transport. Carbon can fairly improve the electrical conductivity of the LiFePO_4 , but it comes at a price because Li-ions should diffuse through a carbon membrane, which might not be easy depending on the carbon structure. In fact, increasing the rate of the electron transfer is not beneficial if slowing down the Li-ion transport. The electron transport rate, which is represented by the LiFePO_4 electrical conductivity, is normally the rate-limiting process; but sufficient improvement in the electrical conductivity can change the situation in which the Li-ion transport is the rate-limiting process. Since the charge balance is essentially required, it is useless to improve one of these processes while the other is lagging behind. Therefore, it is useful to use an extra agent to contribute to the ionic conductivity [230].

Although carbon is a suitable material to improve the SEI formed on the LiFePO_4 , it has been proposed that there are other materials which can do the job better than carbon while the role of carbon for improving the electrical conductivity is still paramount.

In fact, the aim is to utilize an ionic conductor as well as the carbon electron conductor [231–235]. For instance, decorating the LiFePO_4/C with nano-sized Si nanoparticles can noticeably reduce the charge transfer resistance and the peak-to-peak separation in the CV of the LiFePO_4/C [230]. Metal oxides are usually common candidates for double coating of LiFePO_4 [73,74].

In a similar context, it has been reported that coating the LiFePO_4/C with TiO_2 reduces the specific capacity but transforming the TiO_2 layer to Ti_2O_3 can significantly improve the specific capacity (from 158 to 185.4 mAh g^{-1}) [235]. Similar results have been reported for decorating the graphene cover by CuO nanoparticles [231].

There are electroactive materials, which can have some synergistic effects and excellent lattice match, improving the integrity of the LiFePO_4 electrode. For instance, covering LiFePO_4 particles with a symbiotic layer of $\text{Fe}_2\text{P}_2\text{O}_7$, which is an anode material with a specific capacity of 490 mAh g^{-1} , before the lateral carbon coating, can additionally improve the battery performance [57]. Since the aforementioned anode material is not electrochemically active at the potential range of LiFePO_4 , it has no noticeable effect on the performance voltage. The key factor is that the overall specific capacity increases by the amount of $\text{Fe}_2\text{P}_2\text{O}_7$ only until 5 wt% and decreases for higher amounts.

In general, anode materials have been commonly used as the surface modifiers to mediate the ion transfer at the electrode/electrolyte interface. Since the primary role of the coating is to improve the electrical conductivity, it has been reported that superconducting materials can be beneficial [236]. In the electrolyte side, ionic liquids are excellent candidates to mediate the ionic conductivity at such interfaces. Different applications of ionic liquids in lithium batteries has been reviewed recently [237]. Yu et al. used ionic liquids as a co-solvent in the hydrothermal synthesis, as the ionic liquids can control the growth of the particles in an ionic oriented medium [106]. However, ionic liquids have not been used to directly mediate the attachment of carbon coating or the Li diffusion process.

Belanger and his coworkers demonstrated that grafting functional groups on the lateral surface of LiFePO_4/C could improve the battery performance at high rates, though the specific capacity of the original LiFePO_4 is higher at low discharge rates [238]. The amount of such functional groups is normally below 1 wt%, and thus, there should be no significant impact on the energy and power density of the full cell. Due to the complicated interference of

these functional groups in the interfacial processes, this phenomenon should be profoundly examined to understand the exact mechanism. Since there are numerous functional groups, which can be possibly used for the surface modification of LiFePO_4/C , there can be promising practical cases.

10. Perspective: what is missing?

There is no doubt that LiFePO_4 is a promising low-cost cathode material for the lithium-ion batteries and carbon coating is an essential process for any practical development. In the electrode structure, the electrical conductivity between the LiFePO_4 particles is poor and utilizing a conductive agent is mandatory. In this direction, carbon is the best choice because of its low cost and the availability of various forms. As a matter of fact, LiFePO_4/C is somehow considered as a well-established cathode material; instead of employing carbon to improve the battery performance of LiFePO_4 . In other words, the focus is on the synthesis of LiFePO_4/C rather than improving the battery performance of a well-established form of LiFePO_4 by various approaches including carbon coating. Direct synthesis of LiFePO_4/C is of practical interest, but since different structures of LiFePO_4 are formed in various available methods for the synthesis of LiFePO_4/C , it is difficult to systematically understand which type of carbon coating can result in better battery performance.

Owing to the fact that the role of carbon is to improve the electrical conductivity between the LiFePO_4 particles, it is not still clear if carbon coating is really improving the Li diffusion within the electroactive material. Both ion and electron transports are slow in the LiFePO_4 cathodes represented by slow Li solid-state diffusion and low electrical conductivity. It is believed that the rate-determining step in a raw LiFePO_4 is the electron transport, which can be enhanced by a carbon coating. The question is whether the Li diffusion has become the rate-determining process in LiFePO_4/C or the electron transport is still rate-determining. The vague point is the nature of the Li solid state diffusion, which has been identified by a low diffusion coefficient in the range of $10^{-14} \text{ cm}^2 \text{ s}^{-1}$. However, the single-particle studies revealed that the Li diffusion within the LiFePO_4 particle can be as fast as that of LiCoO_2 with a diffusion coefficient in the range of $10^{-9} \text{ cm}^2 \text{ s}^{-1}$ [54]. Similar results have been reported for the Li diffusion in single-crystal LiFePO_4 [239]. In this case, the slow diffusion of Li is not within the LiFePO_4 lattice but the electrode structure (*i.e.*, a package of the particles bound by a binder). If using single-crystalline nanomaterial, the diffusion coefficient will be slow again due to the barriers between the LiFePO_4 particles [240–242]. The electrochemical studies of LiFePO_4/C thin films are less complicated due to the shortened diffusion lengths [243,244], but the electrode packing is still based on a random architecture in which the diffusion process cannot be simplified.

11. Prospective: where do we go?

For three decades, LiFePO_4 was a common candidate for the cathode of lithium batteries, and thousands of papers have been published; however, we still have no clear understanding of the diffusion at different places of a LiFePO_4 cathode. There are interesting practical reports in the literature, but we will not be able to design the practical LiFePO_4 cathodes without understanding its needs at the atomic scale to facilitate the electron and ion transports across the cathode material. Based on the surveys made in this review, it is aimed to highlight the lacking knowledge, which could lead us to a better understand of the LiFePO_4/C system.

11.1. Single-particle electrode

Since the general tendency is to find the most practical cathode material made of LiFePO_4 , most studies employ a practical cell, and there is less attention to fundamental studies. There are only a few studies of LiFePO_4 based on single-particle or single-crystal electrodes. Investigating the Li diffusion within the LiFePO_4 single-particles with different structures and morphologies can provide a profound insight into the real mechanism of the Li diffusion, which is significantly slowed down in packed electrodes. Although there is no interconnection between the LiFePO_4 particles in a single-particle electrode, still carbon coating can reveal important information about the carbon/electrolyte and carbon/ LiFePO_4 interfaces as well as the permeability of the carbon layer.

11.2. Single-crystal electrode

Numerous LiFePO_4/C electrodes have been prepared with various methods in which both LiFePO_4 and carbon were different from other reports. A key point in designing the LiFePO_4/C materials is to understand the internal interface. Employing a single-crystal electrode provides an opportunity to inspect the interface formed by carbon on a well-defined electroactive material. In this case, it is possible to inspect the ionic permeability of the carbon layer and the requirement of an additional ionic conductive agent.

11.3. Single-particle single-crystal electrode

The best sample for subtly investigating the electrochemistry of LiFePO_4 and subsequently LiFePO_4/C is to use a single-crystal single-particle as the cathode. In this case, the fastest possible solid-state diffusion through the LiFePO_4 cathode can be inspected.

11.4. Ultra thin LiFePO_4/C film electrode

If preparing an ultra-thin film of LiFePO_4 (*e.g.*, thinner than 100 nm) and coating its surface with a carbon layer; it is possible to inspect the interfacial nature of the carbon layer on both sides. Hence, powerful surface techniques can be directly employed to fully understand the nature of the LiFePO_4/C interface.

11.5. In-situ and ex-situ inspection of Lithiation and delithiation

When a specific capacity higher or even close to the theoretical capacity is achieved for a LiFePO_4/C , it is vital to inspect the lithiation and delithiation by elemental analysis and crystallographic techniques. It is of utmost importance to find where exactly the excess lithium is stored.

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