

Urgency of LiFePO_4 as cathode material for Li-ion batteries

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Abstract. The energy crisis involving depletion of fossil fuel resource is not the sole driving force for developing renewable energy technologies. Another driving force is the ever increasing concerns on the air quality of our planet, associated with the continuous and dramatic increase of the concentration of greenhouse gas (mainly carbon dioxide) emissions. The internal combustion engine is a major source of distributed CO_2 emissions caused by combustion of gasoline derived largely from fossil fuel. Another major source of CO_2 is the combustion of fossil fuels to produce electricity. New technologies for generating electricity from sources that do not emit CO_2 , such as water, solar, wind, and nuclear, together with the advent of plug-in hybrid electric vehicles (PHEV) and even all-electric vehicles (EVs), offer the potential of alleviating our present problem. Therefore, the relevant technologies in LiFePO_4 as cathode material for Li-ion batteries suitable to the friendly environment are reviewed aim to provide the vital information about the growing field for energies to minimize the potential environmental risks.

Keywords: LiFePO_4 ; cathode material; Li-ion batteries; nanotechnology

1. Introduction

The three principal alternatives to fossil fuels as an energy source are nuclear, solar, and wind energy. Each of these requires energy storage, and the most versatile way to store energy is as chemical energy. Therefore, the major challenge ahead is the development of effective electronic energy storage (EES) systems (Basic research needs for electronic energy storage 2007, Wikipedia encyclopedia, Goodenough 2007, Armand and Tarascon 2008). Today's EES devices, typically chemical storage (batteries) or electrochemical capacitors (ECs), are not capable of meeting the increasing demand, not to mention the energy storage requirements of the coming future. Portable EES in the form of rechargeable batteries powers the wireless revolution in cellular telephones and laptop computers. With some technical problem solved, it is now enabling the successful development of hybrid electric vehicle (HEV). These developments have stimulated an international race to achieve the PHEV (plug-in hybrid electric vehicles), which would allow commuters to drive to work solely by stored electric power charged from the grid during off-peak hours. However, current battery technology provides only limited vehicle performance and driving range-fewer than 50 miles between charging cycles. Enhanced EES devices are needed to make

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PHEVs practical means for efficient and reliable transportation. EES will also be critical for effective around-the-clock delivery of electricity generated from solar, wind, or nuclear sources. For example, EES devices will be required to store electricity generated from solar sources to be used at night. Because energy usage peaks during the day, electricity generated during low-demand periods at night needs to be stored efficiently for use during peak demand. This can reduce the number of generators required, thus the cost. EES devices are also needed to mitigate short-term fluctuations in power, which represent a major problem in the current electronic supply grid (Tollefson 2008). Current EES systems fall far short of meeting these future electronic energy supply needs. Without these advanced EES systems, the transition to emerging technologies for alternative (non-CO₂ generating) electricity generation will not be realized. The efficient generation and use of clean electricity is vital for the future; hence, EES is viewed as a critical technology (Basic research needs for electronic energy storage 2007, Goodenough 2007, Armand and Tarascon 2008).

Furthermore, in addition to large-scale application such as electric vehicles and backup power stations, batteries must also be developed to satisfy recent advances in microelectronics. These require miniature power sources, such as solid-state lithium-based thin-film batteries (Armand and Tarascon 2008, Bates *et al.* 2000).

2. Advantages of Li-ion batteries

A battery composed of several electrochemical cells that are connected in series and/or in parallel to provide the required voltage and capacity. Each cell consists of a positive and a negative electrode (both are sources of chemical reaction) separated by an electrolyte containing dissociated salts solution, which enable ion transfer between the two electrodes. Once these electrodes are connected externally, the chemical reactions proceed simultaneously at both electrodes, thereby liberating electrons and enabling the current to be tapped by the user. The amount of electronic energy, expressed either per unit of weight (W h kg^{-1}) or per unit of volume (W h l^{-1}), that a battery is able to deliver, is a function of the cell potential (V) and capacity (A h kg^{-1}), both of which are linked directly to the basic chemistry of the system (Armand and Tarascon 2008, Tollefson 2008, Wakihara and Yamamoto 1998, Tarascon and Armand 2001).

Hundreds of electrochemical couples have been up to now proposed, the most notable primary battery being Zn-MnO₂, with lead-acid, Ni-Cd, nickel metal hydride and lithium ion being the most common secondary types. The first-generation EVs deployed lead-acid battery, which is still the technology of choice for conventional vehicles. Lead-acid batteries are safe, cheap, long-lived and reliable, but they are also big, heavy and contain toxic element (Pb). A second-generation vehicle released in 1999 (Toyota Prius) featured a nickel metal hydride battery. These batteries pack more power than standard lead-acid ones but can be permanently damaged if over-discharged. To maintain an adequate safety margin, Toyota limited the Prius to use only 20% of its battery charge during normal operation. The best path in long term, however, would be all-electric vehicles that could finally eliminate oil consumption. Getting rid of the petrol motor greatly lessens costs and complexity, and opens up space for more battery power. Lithium-ion batteries, which are compact and have a high capacity, are natural starting materials (Armand and Tarascon 2008, Tollefson 2008, Wakihara and Yamamoto 1998, Tarascon and Armand 2001).

A lithium-ion battery consists of a lithium-ion intercalation negative electrode (generally graphite), and a lithium-ion intercalation positive electrode (generally the lithium metal oxide, i.e.,

LiCoO_2), being separated by a lithium-ion conducting electrolyte, for example a solution of LiPF_6 in ethylene carbonate-diethylcarbonate as well as a polymer separator (Celgard) (Arico 2005). Among the various existing technologies, Li-based batteries, currently outperform other systems in powering most of today's consumer electronics such as laptop computers, digital cameras, as well as cellular phones because of their high energy density and design flexibility. Moreover, they have been intensively studied for use as power supplier of EVs and HEVs. This explains why they receive most of the attention at both fundamental and applied levels (Wakihara and Yamamoto 1998, Whittingham 2004, Balbuena and Wang 2004).

3. Merits of LiFePO_4 as cathode material for Li-ion batteries

The batteries used in EVs require high energy as well as high power density (i.e., the ability to charge and discharge very fast). There are three major types of lithium ion cells based on different cathode materials. They are layered lithium transition metal oxide (typified by LiCoO_2) (Mizushima *et al.* 1980), spinel lithium manganese oxide (LiMn_2O_4) (Thackeray *et al.* 1983) and olivine lithium iron phosphate (LiFePO_4) (Padhi *et al.* 1997a, b).

LiCoO_2 has the $\alpha\text{-NaFeO}_2$ structure with the oxygen in a cubic close-packed arrangement (Amatucci *et al.* 1996, Whittingham 2008, Thackeray 2002). On complete removal of the lithium, the oxygen layers rearrange themselves to give hexagonal close packing of the oxygen in CoO_2 (Amatucci *et al.* 1996). Between these composition limits several phases are formed with varying degrees of distortion of the ccp oxygen lattice. The lithium ion battery based on lithium cobalt oxide cathode has a very high energy density (gravimetric energy densities as high as $120\text{-}150\text{ Wh kg}^{-1}$, two to three times those of usual Ni-Cd batteries) because of its high voltage (4 V) and moderate specific capacity. Current light-weight, compact, and high energy density rechargeable batteries have been realized through the discovery of this oxide. However, it suffers from limited resources, toxicity, and safety concerns (Whittingham 2004, Whittingham 2008).

The structure type of LiMn_2O_4 is defect spinel, in which Mn ions occupy the octahedral sites, while Li^+ resides on the tetrahedral sites. The spinel LiMn_2O_4 , although possessing $\sim 10\%$ less capacity than LiCoO_2 , has an advantage in terms of cost, high rate capability, safety characteristics, and is perceived as being 'green' (that is, non-toxic and from abundant material source) (Thackeray *et al.* 1983). Its implementation has been delayed because of its limited cycling capability, and its poor storage performances at elevated temperatures. In addition, this material has been plagued by self-discharge when left fully charged, particularly at elevated temperatures (Tarascon and Armand 2001, Whittingham 2004).

LiFePO_4 occurs in nature as the mineral triphylite, crystallized in an olivine-type structure (space-group: $Pnma$) having the oxygen atoms arranged in a slightly distorted, hexagonal close-packed arrangement (Padhi *et al.* 1997a, b). The phosphorous atoms occupy tetrahedral sites, while the iron and lithium atoms occupy octahedral sites denoted as M(2) and M(1), respectively. The FeO_6 octahedra are linked through common corners in the bc -plane, and the LiO_6 octahedra form edge-sharing chains along the b -axis. One FeO_6 octahedron has common edges with two LiO_6 octahedra and a PO_4 tetrahedron. The PO_4 groups share one edge with an FeO_6 octahedron and two edges with LiO_6 octahedra (Fig. 1) (Tarascon and Armand 2001).

Lithium iron phosphate cell has a discharge potential around 3.4 V vs lithium, higher energy density of 170 mAhg^{-1} as compared with 140 mAhg^{-1} for the LiCoO_2 , (comparable to stabilized LiNiO_2), excellent calendar cycling stability of up to 2000 cycles and good availability due to the

abundant Fe resources in nature (Tarascon and Armand 2001). Most importantly, electrochemical extraction of lithium from the LiFePO_4 phase is accompanied by a direct transition to the isostructural FePO_4 (heterosite) phase, in which the Fe^{2+} ions are oxidized to Fe^{3+} , leaving the olivine framework intact. Thus there is no structural change upon lithium insertion and extraction. The Fe-P-O bonds in LiFePO_4 are stronger than the Co-O bonds in LiCoO_2 and thus the oxygen atoms are much harder to remove which consequently leads to a higher stability upon short-circuit, overheating, etc. Only under extreme heating (generally over 800 °C) breakdown occurs.

Therefore, LiFePO_4 is intrinsically more stable against overcharge or short circuit conditions and has the ability to withstand high temperature operation without decomposing, firing or explosion that sometimes would happen in LiCoO_2 batteries. As a result, LiFePO_4 technology possesses excellent safety characteristics which are critically important for EVs and are fundamentally superior to other types of lithium-ion batteries. Furthermore, LiFePO_4 does not contain any toxic elements. The advantages of traditional lithium-ion coupled with the safety features of phosphates, make LiFePO_4 technology the most promising power supply for the future EVs (Table 1).

4. Problems encountered and solutions proposed for LiFePO_4

In the lithium metal oxides with either a layered (LiMO_2 , M = Co, Ni, Mn) or a spinel (LiM_2O_4 , M = Mn, Ni) structure, a cubic-close-packed oxygen array provides an edge-sharing network of octahedra for the transition metal ions (Thackeray 2002). These materials are good lithium-ion conductors and they both have inherent good electronic conductivity, two attributes that are essential for providing cells with acceptable energy and power. In particular, the presence of mixed-valent cations, for example, $\text{Co}^{4+/3+}$ ions in $\text{Li}_{1-x}\text{CoO}_2$ and $\text{Mn}^{4+/3+}$ in $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$ for $0 < x < 1$ contributes significantly to the inherent electronic conductivity of the electrodes during charge and discharge. In these structures, electron transfer occurs between the mixed-valent cations on the edge-shared octahedral array. By contrast, the cation arrangement in olivine structure typified by LiFePO_4 differs significantly from that in the layered and spinel structures (Fig. 1). There is no continuous network of FeO_6 edge-shared octahedral that might contribute to electronic conductivity; instead, the divalent Fe^{2+} ions occupy corner-shared octahedra. During the electrochemical lithium insertion and extraction, the resulting phases, LiFePO_4 and FePO_4 , are both poor electronic conductors because they each contain Fe cations with only one oxidation state (2+ or 3+, respectively). Therefore, the olivine-type LiFePO_4 cathode materials encounter the principal drawback of poor rate capability resulting from its inherent low electronic conductivity ($10^{-9} \sim 10^{-10} \text{ S.cm}^{-1}$) and low Li^+ ions diffusion rate. This shortcoming has largely hindered its wide application (Whittingham 2004, Thackeray 2002).

To make commercial implementation of LiFePO_4 materials, in the past few years, tremendous academic efforts have been devoted to tackle the poor rate problems. The important approaches for enhancing the real electronic conductivity include (1) surface coating of the LiFePO_4 particles with a thin layer of conductive material (carbon (Ravet *et al.* 2001, Chen and Dahn 2002, Wilcox *et al.* 2007), silver (Park *et al.* 2004, Mi *et al.* 2008, Chen *et al.* 2004, Croce *et al.* 2002), or copper (Caballero *et al.* 2006, Morales *et al.* 2007)); (2) making homogeneous composites with conductive polymers, for instance polyacene (PAS) (Xie *et al.* 2006) and polypyrrole (PPy) (Huang and Goodenough 2008, Wang *et al.* 2008, Huang *et al.* 2006, Park *et al.* 2007); (3) formation of nano-or micro-porous structured LiFePO_4/C particles by using sol-gel methods

(Dominko *et al.* 2005, Dominko *et al.* 2007) and (4) surface nano-connection of highly conductive inorganic layers such as Fe_2P (Herle *et al.* 2004, Rho *et al.* 2007) and RuO_2 (Hu *et al.* 2007). Another approach to increase the conductivity is aliovalent doping as proposed by Chiang and co-workers (Chung *et al.* 2002, Meethong *et al.* 2009). However, doping may have deleterious impact if it occurs on the lithium sites. On the other hand, fabricating ultrafine LiFePO_4 nanoparticles with specific platelet shape and uniform size distribution via wet-chemical routes was also proved to be a feasible method to enhance the Li^+ diffusion rate (Yamada *et al.* 2001, Delacourt *et al.* 2006).

The problems of low electronic conductivity and slow diffusion of lithium ions in LiFePO_4 can be further alleviated by coating it with conductive species and minimizing particle size simultaneously, for example, a nanocomposite of LiFePO_4 with a carbon xerogel could be formed from a resorcinol-formaldehyde precursor (Huang *et al.* 2001). This nanocomposite achieves 90% theoretical capacity at $C/2$ with very good stability at room temperature. Such excellent electrochemical performance is attributed to modification with carbon and control of particle size to nanometer scale. Both factors are of essential importance. Quite recently, Ceder *et al.* from MIT, based on phase diagram, reported a fast Li^+ ion conducting phase (Fe^{3+} -containing $\text{Li}_4\text{P}_2\text{O}_7$ -like phase) prepared by a controlled off-stoichiometry method on the surfaces of LiFePO_4 particles of less than 50 nm to display a rate capability equivalent to full battery discharge in 10-20 s (surprisingly as high as 400 °C) (Kang and Ceder 2009).

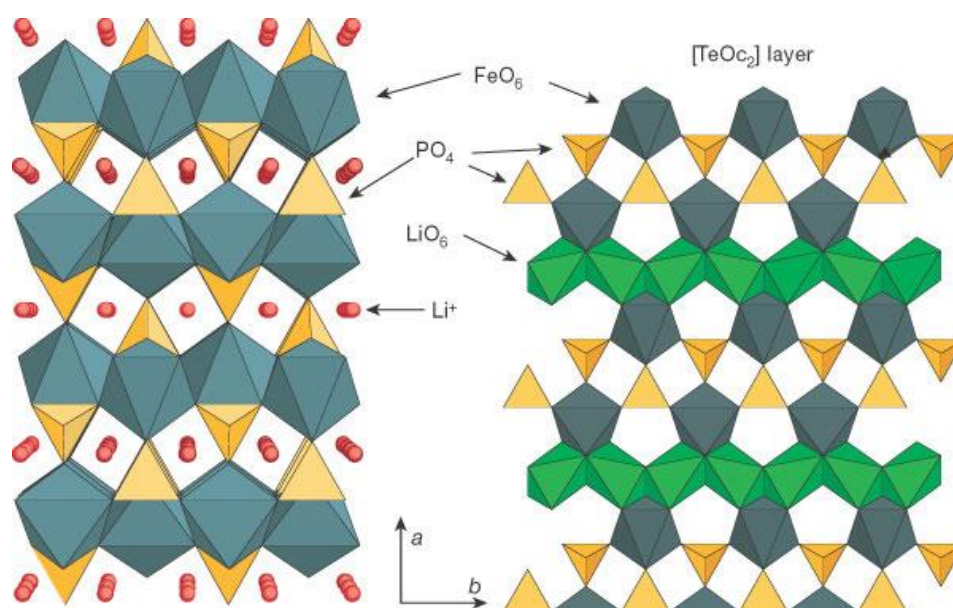


Fig. 1 The crystal structure of olivine LiFePO_4 in projection along $[001]$. On the left, expanded view of the framework built from the corner-shared FeO_6 octahedra and PO_4 tetrahedra, with Li ions in red. On the right, restricted view of Li, Fe and P distribution between two distorted, *h.c.p.* (hexagonal close packed) oxygen-dense layers ($\text{P}_{\text{Td}}[\text{LiFe}]_{\text{oct.}}\text{O}_4$). The lithium ions are octahedrally coordinated to oxygen, forming edge-sharing chains of LiO_6 octahedra and Li ions may diffuse along $[010]$ and $[001]$ (Tarascon and Armand 2001)

Table 1 Comparison data among various lithium ion batteries

Battery	LiFePO ₄	LiCoO ₂	LiMn ₂ O ₄	Li(NiCoMn)O ₂
Safety	Safest	Not Stable	Acceptable	Not Stable
Environmental Concern	Green	Toxic	Green	Toxic
Cycle Life	Excellent	Acceptable	Normal	Acceptable
Power/Weight Density	Acceptable	Good	Acceptable	Best
Long Term Cost	Low	High	Acceptable	High
Temperature Range	Excellent (-20°C to 70°C)	Decay beyond (-20°C to 55°C)	Decay extremely fast over 50°C	-20°C to 55°C
Rate Capability	Acceptable	Good	Good	Good

5. Remaining issues leading to the present studies

5.1 Remaining transport issues

In spite of the very successful approaches marrying harmoniously particle size reduction and carbon coating, numerous questions remain to be answered concerning the fundamental origin of the kinetic limitations and failure. Before Li-batteries based on LiFePO₄ could be fully implemented in a wide range of applications from portable electronics to hybrid electric vehicles, fundamental research is critically needed to uncover the underlying principles that govern these complex and interrelated processes, starting with the transport issue. Indeed, such investigations have been the subject of many studies and of a debate on the importance of ionic versus electronic conductivity. The Li ions diffusion mechanism during the electrochemical charge and discharge also remained to be uncertain.

Attempts to understand what is going on in lithium deintercalation/intercalation in Li_xFePO₄, numerous studies have been devoted to establish the relation between the structure and the ionic and electronic transport properties. The theoretical studies on *ab initio* calculation by Ceder's group (Morgan *et al.* 2004, Wang *et al.* 2007) and then by Islam *et al.* 2007 have shown that lithium ions can move easily only in the tunnels parallel to the *b* direction, which was later experimentally confirmed by Yamada *et al.* (Nishimura *et al.* 2008) using high temperature powder neutron diffraction coupled with maximum entropy method. However, Maier *et al.* showed that the electronic conductivity, ionic conductivity, and chemical diffusivity of Li⁺ are essentially two-dimensional (*b-c* plane) in a LiFePO₄ single crystal (Amin *et al.* 2007).

Various models have been proposed to elucidate the lithium intercalation/deintercalation mechanism, which, unfortunately, turns out to be controversial. The first one is the so-called "core-shell" model (Srinivasan and Newman 2004) based on conventional bulk sample (micrometer scale in size and irregular in shape, but simplified as spherical). This model assumes a growing shell of one phase (LiFePO₄) surrounding a shrinking core of the other phase (FePO₄) during Li insertion (battery discharging), and an FePO₄ shell surrounds a LiFePO₄ core during Li extraction (battery charging) (Padhi *et al.* 1997b, Srinivasan and Newman 2004). Recent electron microscopy studies on the 50 % delithiated crystallites with hexagonal platelet-like particle shape (dimension: 4×2×0.2 μm), however, have showed that there are alternating domains of intercalated and deintercalated phases with intermediate zones where defects are concentrated (Chen *et al.* 2006). The mosaic model (Andersson and Thomas 2001) (based on micrometer scale sample)

takes into account the possibility of the extraction/insertion of lithium to start at different nucleation sites. The question as to whether these nucleation sites are located at several points on the crystal surface or are more distributed below the surface is still unknown. More recently, an electron energy-loss spectroscopy (EELS) study on thin platelet-type particles with an average size of ca. 140 nm carried out by Laffont *et al.* (2006) confirmed that the shrinking core–shell model is not relevant to explain lithium deintercalation/intercalation in the olivine structure owing to the strong anisotropy of lithium diffusion. From the EELS results, they showed that the nanometer interface between single-phase areas composed of LiFePO_4 or FePO_4 is the juxtaposition of the two end members.

The common feature among all previous models is that they assume the existence of an interface, i.e. the coexistence of LiFePO_4 and FePO_4 regions inside each particle. This is now challenged by a new domino-cascade model (Fig. 2), according to which the growth reaction is considerably faster than its nucleation and consequently the individual LiFePO_4 nanoparticles (with a diameter close to 100 nm) should be either fully intercalated or fully deintercalated (Delmas *et al.* 2008).

5.2 Importance of controlling particle shape and size

The development of high-performance lithium-ion batteries can benefit from the advantageous characteristics of nanomaterials, such as high surface areas, short diffusion paths, large quantities of active sites, as well as freedom for volume change during charging–discharging cycles (Wang and Cao 2008). Many groups have explored the advantages of nanosized LiFePO_4 . Masquelier *et al.* have reported that the well-established two-phase insertion process in LiFePO_4 electrodes at room temperature could be changed into a single-phase insertion process by reducing the particle size down to 40 nm via low temperature precipitation method (Gibot *et al.* 2008). Meethong *et al.* have shown that decreasing the particle size to below 50 nm could significantly extend the solid solutions in the vicinity of LiFePO_4 and FePO_4 , therefore enhancing the lithium mobility (Meethong *et al.* 2007a, b, Kobayashi *et al.* 2009). On the other hand, accompanying the reduction of particle sizes to nanoscale, the influence of surfaces and interfaces that are largely governed by the particle morphology can no longer be neglected in the rationalization and prediction of material thermodynamic and kinetic properties. Recently Wagemaker *et al.* (2009) have studied the interface contribution on equilibrium compositions for two-phase (Li^+ -poor heterosite $\text{Li}_\alpha\text{FePO}_4$ phase and Li^+ -rich triphylite $\text{Li}_{1-\beta}\text{FePO}_4$ phase) coexistence in nanocrystallite with three basic particle geometries shown in Fig. 3: rectangular, spherical and diamond-shaped, based on the typical values of surface and interface energies estimated from the first principles method for Li_xFePO_4 . They predicted that not only do the solubility limits and equilibrium compositions depend on the particle size, they are also surprisingly sensitive to the particle shape. It has been unambiguously proved from other nanocrystallite materials that morphological control is becoming increasingly important, as many of the properties are highly shape and size dependent (Xia *et al.* 2003, Fisher and Islam 2008). It is expected that the contradiction between the aforementioned varying transport models might actually come from the variations on the particle size, morphology as well as surface chemistry of different samples studied.

5.3 State-of-art synthesis of LiFePO_4 nanostructures

A range of synthesis techniques has been used to prepare LiFePO_4 with a variety of particle

morphologies and size distributions. For example, Masquelier *et al.* have reported a low temperature precipitation process under atmospheric pressure for the direct synthesis of carbon-free LiFePO₄ nanocrystallites with spherical (diameter centered at ca. 140 nm) and thin plate-like morphology (width: 15 nm, length: 60 nm) as shown in Fig. 4. The synthesized carbon free 140 nm spherical nanopowers displayed very nice rate capability (147 mAh/g at 5°C) (Delacourt *et al.* 2006). And most interestingly, the ultrafine plate-like nanoparticles exhibited sloping voltage charge/discharge curves, characteristic of a single-phase behavior in sharp contrast with the traditional two-phase feature in olivine LiFePO₄ (Gibot *et al.* 2008).

Chen *et al.* (2006) have prepared a typical thin hexagonal plate-like LiFePO₄ crystals by a hydrothermal method. Interestingly, the large faces that constitute nearly 80% of the exposed surfaces lie normal to the *b* axis, which is believed to be the most favorable direction for Li⁺ diffusion. Therefore such unagglomerated plate-like morphology with large *ac* faces substantially increases the active area and decreases the diffusion distance for Li⁺ ions, thereby improving both rate capability and utilization of the active materials. Moreover, they have elucidated the mechanism by which LiFePO₄ is transformed into isostructural FePO₄ based on HRTEM observations. In the 50% oxidized sample, ordered domains of FePO₄ spaced between the parent LiFePO₄ domains were observed. The phase boundary transformation proceeded in the direction of the *a*-axis at dislocation lines running parallel to the *c*-axis. In the light of this work, ultrafine plate-like LiFePO₄ nanocrystallites have been synthesized by several groups using methods like microwave assisted solvothermal (Murugan *et al.* 2008, Saravanan *et al.* 2009), direct precipitation (Gibot *et al.* 2008) and polyol process (Lee *et al.* 2009).

LiFePO₄ nanowires have been synthesized via a surfactant (NTA: nitrilotriacetic acid) assisted hydrothermal method (Wang *et al.* 2009). Similarly, needle-like LiFePO₄ nanocrystallites have also been synthesized by ionothermal (Recham *et al.* 2009b) and hydrothermal techniques (Dokko *et al.* 2007). LiFePO₄ crystallites have been observed in the shape of rectangular prism (Recham *et al.* 2009b), spindle (Dokko *et al.* 2007, Chen *et al.* 2007, Yang *et al.* 2001), diamond (Chen *et al.* 2007, Recham *et al.* 2009a, Dokko *et al.* 2006), block (Recham *et al.* 2009b, Dokko *et al.* 2007, Chen *et al.* 2007, Franger *et al.* 2003, Ellis *et al.* 2007), spherical (Xu *et al.* 2008, Wang *et al.* 2008) as well as bundle-like (Dokko *et al.* 2007, Chen *et al.* 2007, Franger *et al.* 2003, Yang *et al.* 2009).

Reduction of transport distance has also been tried from other aspect, forming a microporous or mesoporous structure inside the large primary LiFePO₄ particles (Dominko *et al.* 2007, Lim *et al.* 2008, Gaberscek *et al.* 2005, Doherty *et al.* 2009, Gaberscek *et al.* 2007). As the pores are formed due to vigorous gas evolution (mainly CO and CO₂) during degradation of a citrate precursor, they are perfectly interconnected within each particle. Conductive carbon, the byproduct of citrate degradation, is *in-situ* deposited on the walls of the emerging pores. The superposition of a continuous 1-2 nm thick carbon film (electron conductor) on pores (ion conductor when filled with electrolyte) represents a unique particle interior. The as-prepared porous materials can operate at current rates up to 50°C while preserving a high tap density of ca. 1.9 g cm⁻³ (Dominko *et al.* 2007, Gaberscek *et al.* 2005, Gaberscek *et al.* 2007). This novel concept substantially solves the problem of making dense films encountered in nanoparticles. Doherty *et al.* 2009 have presented a solution-based colloidal crystal templating method to produce hierarchically porous LiFePO₄ electrode materials. The well-stacked poly methyl methacrylate (PMMA) colloidal crystals provided robust scaffolding for the condensation as well as crystallization of LiFePO₄. Once the PMMA spheres were removed through high temperature calcinations under inert atmosphere, the crystallized LiFePO₄ featured an open lattice structure with residual carbon left over from the decomposed colloidal crystal templates. The high surface area materials allowed good electrolyte

access to the LiFePO_4 active sites and therefore enhanced electrochemical properties (160 mAh/g at 0.1°C and 115 mAh/g at 5 °C).

Another interesting type of nanostructure is thin film electrodes with thickness ranging from a few to hundreds of nanometer via physical or chemical deposition techniques (Sun *et al.* 2009, Matsumura *et al.* 2008, Chiu *et al.* 2008, Sauvage *et al.* 2008a, b, Li and Fu 2007, Hong *et al.* 2007, Song *et al.* 2006, Iriyama *et al.* 2004, Sauvage *et al.* 2004). In addition to their potential application in microbatteries, thin film electrodes are also appealing for fundamental research because, being free of binders and having very specific texture (highly oriented growth), they are simplified system for investigating the basic transport issue.

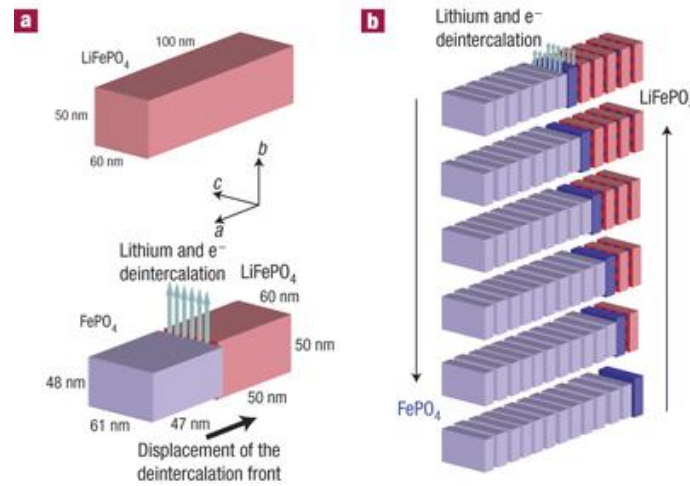


Fig. 2 Schematic view of the ‘domino-cascade’ mechanism for the lithium deintercalation/intercalation mechanism in a LiFePO_4 crystallite. (a) Scheme showing a view of the strains occurring during lithium deintercalation. (b) Layered view of the lithium deintercalation/intercalation mechanism in a LiFePO_4 crystallite (Delmas *et al.* 2008)

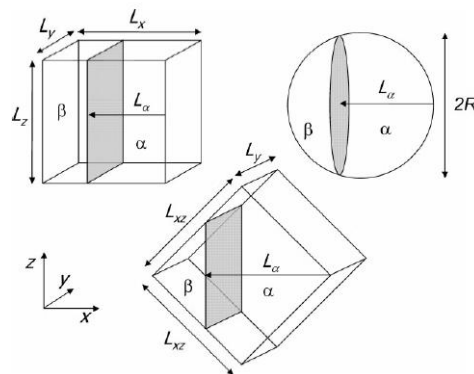


Fig. 3 Particle geometries studied, where the gray surface indicates the orientation of the interface between the two phases α and β . L_α determines the position of the interface (Wagemaker *et al.* 2009)

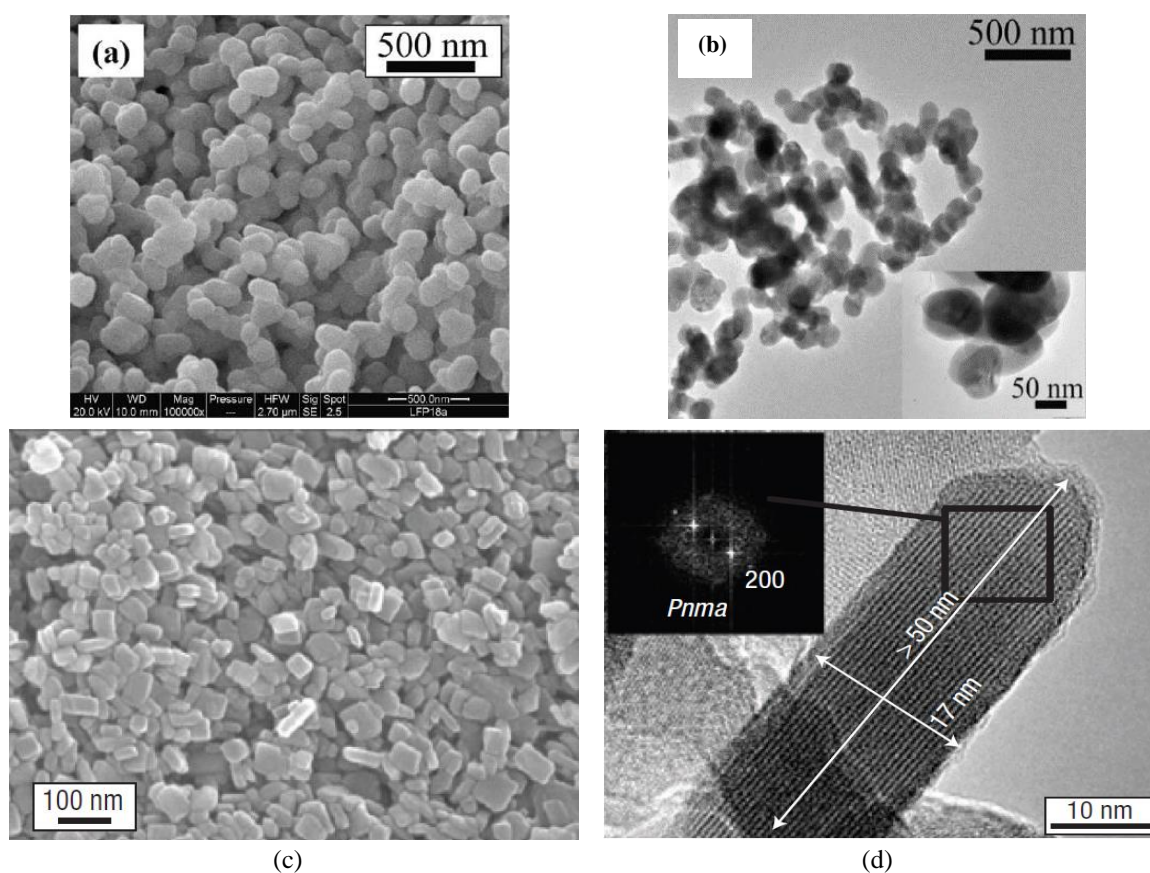


Fig. 4 (a), (c) SEM, (b) TEM and (d) HRTEM images of the carbon-free LiFePO_4 nanoparticles with (a), (b) spherical and (c), (d) thin plate-like morphology via precipitation method (Gibot *et al.* 2008)

6. Conclusions

To improve the rate performance of LiFePO_4 cathode material, the novel nanostructures should be investigated and developed. To achieve this goal, three aspects of research should be pursued

- The preparation of nano thin-film type electrodes.
- The synthesis and electrochemical characterization of LiFePO_4 crystallites with various morphologies and then the study of the co-relationship between particle morphology and electrochemical performance.
- The investigation of growth mechanism of the novel hollow structured LiFePO_4 crystallites that exhibits advantageous rate capability.

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