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LiFePO₄ Cathode Material

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1. Introduction

Rechargeable batteries have largely replaced primary cells as they save resource and reduce pollution. Recent increases in demand for oil, with the associated environment sustainable issues are continuing to exert pressure on an already stretched and strained world energy infrastructure. Clean and efficient energy production from renewable sources is wanted in our energy and environment-conscious society. Among the secondary batteries, lead batteries and NI-MH batteries have stepped back from market since a new and strong system comes into our sight, Li-ion batteries. Li-ion batteries meet what we need. High capacity, high electrochemical potential, superior energy density, durability, as well as the flexibility in design, all the above outstanding properties accelerate the substitution of conventional secondary batteries. They are now prevailingly used in portable electronic devices, 57.4% of sale on mobile phone, 31.5% on notebook computer and 7.4% on camera. Their application has also been extended over other fields, including hybrid electric vehicle, space application, military vehicle et al. The differences between various batteries are exhibited in Tab.1.

cathode	Li-ion	Pb-Acid	Ni-Cd	Ni-MH
lifetime/cycle	500~1000	200~500	500	500
Working potential/V	3.6	1.0	1.2	1.2
Specific energy/Wh kg ⁻¹	100	30	60	70
Specific energy/Wh L ⁻¹	240	100	155	190

Table 1. The comparison between various batteries

cathode	LiFePO ₄	LiFePO ₄ +5%C	LiMn ₂ O ₄	LiCoO ₂	LiNi _{0.8} Co _{0.2} O ₂
Density/g cm ⁻³	3.60	3.48	4.31	5.10	4.85
Potential/V	3.50	3.50	4.05	3.90	3.6
Specific capacity /mAh g ⁻¹	169	159	148	274	274
Specific energy /Wh g ⁻¹	0.59	0.56	0.56	0.98	0.98

Table 2. Electrochemical parameters of several cathode materials

LiCoO₂ is first chose to work as cathode materials when Li-ion batteries come out in 1990. Its long history supports LiCoO₂ a big progress. During that process, other cathode materials are discovered, LiNiO₂, LiMn₂O₄, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, LiFePO₄ et al. Comparisons of electrochemical parameters of several cathode materials are listed in Tab.2.

Each of them has their own characteristics. For example, LiCoO₂ is costly and toxic, and its resource is no longer abundant (A. G. Ritchie, 2001). LiMn₂O₄ owns a much lower capacity and inferior cycle stability (Yuan Gao & Dahn J. R, 1996). Iron-based compounds look attractive as Fe is abundant, inexpensive, and less toxic than Co, Ni, or Mn. The phospho-olivine LiFePO₄ is currently under extensive studies due to its low cost, low toxicity, high thermal stability and high specific capacity of 170mAhg⁻¹. Reduced reactivity with electrolytes results in the very flat potentials during charge-discharge processes.

The potential of material is partly decided by the Fermi level (A. K. Padhi et al, 1997). Much lower Fermi level is wanted to attain a higher working voltage. Among the iron-based compound, especially in LiFePO₄, (PO₄)³⁻ lowers the Fe³⁺/Fe²⁺ redox energy to useful levels. Strong covalent bonding within the polyanion (PO₄)³⁻ reduces the covalent bonding to the iron ion, which lowers the redox energy of iron ion. The Fe³⁺/Fe²⁺ redox energy is at 3.5 eV below the Fermi level of lithium in LiFePO₄. The lower is the Fe³⁺/Fe²⁺ redox energy and the higher the V vs. lithium for that couple. In LiFePO₄, approximately 0.6 lithium atoms per formula unit can be extracted at a closed-circuit voltage of 3.5 V vs. lithium. The most prominent advantages of LiFePO₄ are (1). The structure of material hardly changes while Li ion intercalation and deintercalation; (2). It holds a long voltage platform.

The working principle of Li-ion battery is revealed in Fig.1. Lithium ions extract from anode to insert in cathode in the discharge process. The route is inversed as charge takes place. FePO₄ is the second phase that is present on electrochemical extraction of lithium from LiFePO₄. The extraction of lithium from LiFePO₄ to charge the cathode may be written as Formula (1) and the insertion of lithium into FePO₄ on discharge as formula (2).

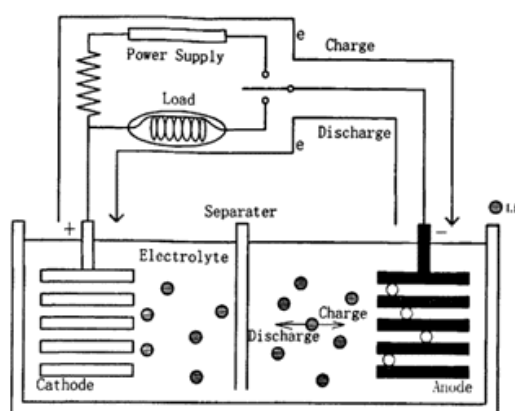
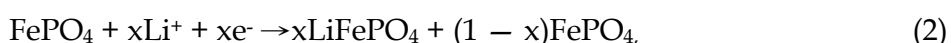
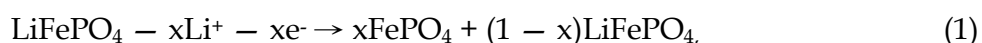


Fig. 1. The schematic diagram of working principle for lithium battery

More efforts are conducted on the investigations of new electrode materials for lithium-ion batteries (Li-ion). The iron based olivine type cathodes (mainly lithium iron phosphate,

LiFePO₄) are regarded as possible alternatives to cathodes based on rare metal composites (i.e. the transition metal oxides LiCoO₂, LiNiO₂).

2. Feature of LiFePO₄

2.1 Crystal structure of LiFePO₄

LiFePO₄ owns an ordered olivine structure, orthorhombic space group *Pnma*. Its systal constants of *a*, *b* and *c* are 1.033, 0.601 and 0.4693μm respectively. Fig.2 and 3 show the crystal structure of LiFePO₄, an ideal model and actual structure. The framework of LiFePO₄ consists of FeO₆-octahedra and PO₄-tetrahedra. FeO₆-octahedra and PO₄-tetrahedra contact each other by sharing oxygen vertices in *b-c* plane. The FeO₆-octahedra then links another PO₄-tetrahedra by sharing a edge. All the PO₄-tetrahedra don't touch each other. Lithium atoms are situated in the interstitial voids of the framework, forming infinite chains along the *c*-axis in an alternate *a-c* plane. Li atoms occupy M1 site and Fe M2 site. The Fe atoms occupy zigzag chains of corner-shared octahedra running parallel to the *c*-axis in the other *a-c* planes. O arranges in terms of hexagonal close packed structure with a slight distortion.

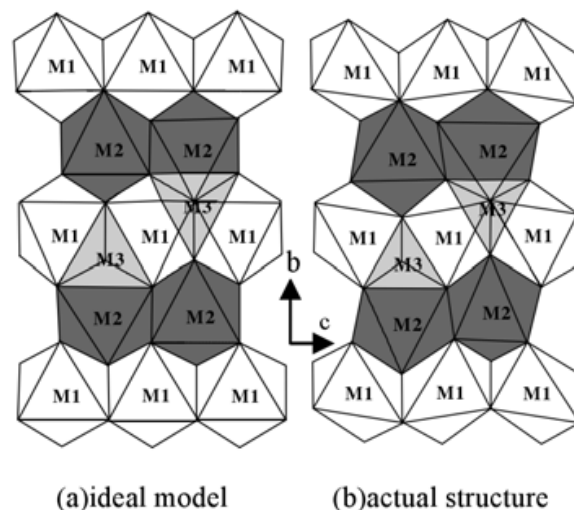


Fig. 2. Crystal structure of LiFePO₄ (a) ideal model and (b) actual structure.

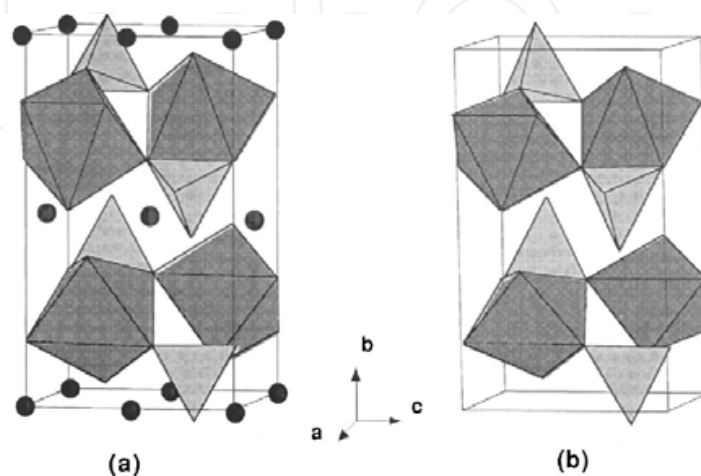


Fig. 3. Crystal structure of (a) LiFePO₄ and (b) FePO₄

The strong P-O covalent bond forms the 3D delocalizing chemical bond, herein LiFePO_4 is thermodynamically and dynamically stable even at temperature above 200°C .

A.K.Padhi pointed out that LiFePO_4 and FePO_4 almost possessed the same structure (Fig.3), both of them were of orthorhombic system (A. K. Padhi et al, 1997a, 1997b). The small distinction between the two compounds results in only slight volume change, so then it won't cause crystal structure damage during charge and discharge process. Not like other cathode materials, the unique olivine structure of LiFePO_4 can assure an excellent stability, therefore its lifetime is much longer.

Fig.4 illustrates the theoretical insertion/extraction process of LiFePO_4 which is different from others. During lithium ions insert into a cathode particle (discharge), the surface region of particles becomes lithiated. And a phase interface emerges between two distinct phase regions (a lithiated phase and a delithiated phase region). The interface shrinks with charge process until the particle becomes one phase region. As discharge proceeds, the surface region becomes delithiated. The phase interface between lithiated phase and delithiated phase propagates inwards until disappear so that a complete charge and discharge procedure is finished.

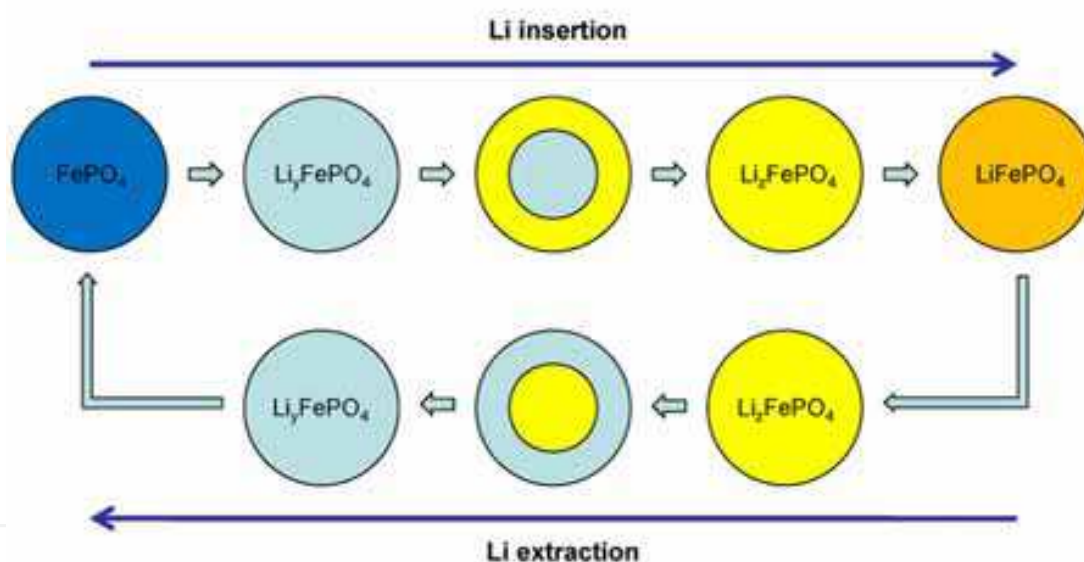


Fig. 4. Complete Li insertion and de-insertion cycle of a spherical LiFePO_4 particle.

That distinct mechanism can explain the phenomenon of super flat voltage plateaus which are related to the surface Li concentration of particles. Since the incoming Li leads only to inner shift of the phase interface, the Li concentration of surface region is constant. That unique flat voltage plateaus are caused by unusual insertion/extraction process of this material.

2.2 Progress in preparing material

LiFePO_4 occurs in nature as the mineral triphylite. However, its impurity could worsen the electrochemistry properties so that triphylite can't be utilized efficiently. Synthesis of LiFePO_4 is another way to obtain better materials. Preparation methods decide the microstructure of compounds which will carry a big weight in the performance of LiFePO_4 .

2.2.1 Solid and liquid state reaction synthesis technology

1. High temperature solid state method

It processes as follows: mix the precursor-salts and lithium salt with a definite ratio, sinter the mixture first at a much lower temperature (300~400°C) to remove volatiles second at a higher temperature (500~800°C) to crystallize LiFePO₄, and then cool, grind and sieve to prepare the product. Solid state reaction method has been a developed technology and been used much frequently since it's simple to synthesis and easy to make mass production. The need for high temperature unfortunately upgrades cost, what's more, the product size always can't be small. So other measures are added to circumvent those problems, such as slightly lowdowning temperature or adding carbon granules.

2. Co precipitation method

Blend the soluble precursor-salts and lithium salt in water, adjust the PH value under N₂ atmosphere with stirring until the mixture react to precipitate LiFePO₄. Filter, wash and dry LiFePO₄ so then dispose it under high temperature. The temperature won't largely affect the microstructure as high temperature solid state method does. This technology needs a shorter reaction time and lower temperature compared with solid state reaction. The particle size can reach the nanometer level and this reduced size can help to enhance the charge-discharge performance especially at big current condition. The inadequacies inhibiting mass production are the complex process and large power consumption.

3. Sol-gel method

Complexing agent helps the Li⁺, Fe²⁺ and PO₄³⁻ to form sol in water solution. Sinter the precipitation of sol-crystal at 400~900°C. The uniform distribution of ions in solution finally acts out a much uniform product that in nanometer size. Monitor the process is easy but industrialization of this technology is hard as the method is complex. Much waste water is produced at last also.

4. Hydrothermal method

The reactions of reactants that dissolve in water proceed in high pressure autoclave at a fixed temperature (<150°C). The product is then watered, filtered and dried to receive pure phase LiFePO₄, in small uniform size just like sol-gel does. This pure phase material can't behave excellent unless be doped with carbon. So then its capacity could reach to 137~160mAh g⁻¹. Rietveld analysis from S. Yang found that 7~8% Fe²⁺ occupy the Li⁺ sites, which is related to the weaker charge/discharge behavior (S. Yang et al, 2002). LiOH as precipitator is added excessively to make sure the completeness of reaction which increases the cost. This system no more needs the protection from inert gas since O₂ is hardly dissolved in water. But operation is on a tiny scale constrained by the manufacture condition.

5. Carbothermal method

J. Barker adopt a new way to synthesize LiFePO₄ with the very inexpensive and readily Fe₂O₃ as available precursor source, instead of FeC₂O₄ et al (J. Baker et al, 2003). The precursors are intimately mixed and pelletized. The reaction mixture is then heated in a tube furnace (at ~750°C) equipped with a flowing Ar atmosphere holding for about 8h. The transition metal reduction and lithium incorporation processes are each facilitated by the high temperature carbothermal reaction based on the transition from C to CO. The Fe³⁺

always can't be deoxidated absolutely and impurities can't be avoided virtually which will have a bad effect on battery performance.

6. High energy ball mill method

The reaction of Ball mill method is driven by the energy generated from steel balls in high speed revolution. A homogeneous solid solution with a small amount of contaminant, coming from the milling equipment, are obtained after 10~24h of high-energy milling of the initial mixture. A single calcination step goes on for no more than 1h. High energy ball mill method (also called Mechanochemical activation) is able to produce homogeneous powders with a particle size in the nanometer range, an increased specific surface area and typically, a high degree of activity. So the discharge capacity of LiFePO_4 can reach 150mAh g^{-1} at rate 0.5C as S.Franger have achieved (S.Franger et al, 2003).

7. Microwave synthesis method

The starting materials are mixed with ethanol in an agate mortar. The mixed powder is dried at $\sim 60^\circ\text{C}$ (lower than that required for furnace heating) and pressed into pellets. Each pellet is covered with glass wool and placed in an alumina crucible with a lid to be heated in microwave oven. Electromagnetic energy is simultaneously absorbed by all parts of precursor so that uniform and rapid heating can be achieved within a short period of time. This distinctive character results in no temperature gradient within all parts. The initial discharge capacity was about 125mA g^{-1} at 60°C by Masashi Higuchi et al which can increased to 161mAh g^{-1} if LiFePO_4 is doped with carbon. (Min-Sang Song et al, 2007) This method can be used together with other synthesis approach so to largely reduce their process time.

8. Pulsed Laser Deposition (PLD)

Thin film electrode can relief the problem of poor conductivity. Pulsed Laser Deposition has been used to fabricate LiFePO_4 thin film electrodes. During the synthesis process of LiFePO_4 , a laser with a fixed wavelength is used in the deposition. The films are deposited on platinum plates or basal planes of highly oriented pyrolytic graphite for minutes at room temperature. The films are then annealed at high temperature for hours under Ar or O_2 gas flow. The electric characters of thin film electrodes can be easily influenced by the articles size and fabrication process. Large particles on the surface of thin film electrode will lead to a bad capacity and poor cycling performance.

9. Electrostatic Spray Deposition (ESD)

A positive voltage of 8.0kV from a direct current power supply is applied to a stainless steel nozzle of a syringe to generate an aerosol. A syringe pump with a definite flowing rate is used to pump the precursor solution. The sample deposited on the substrate by ESD is calcinated at $500\sim 750^\circ\text{C}$ for hours under pure Ar ambient. (A. Yamada et al, 2001) Electrostatic force shatters the solution into small drop of liquid with charge. So then the coulomb repulsion between drops can prevent them from collecting together. Dispersion degree is flexible by adjusting various voltage electrostatic fields. ESD method offers many advantages for thin-film deposition, such as low cost set-up, high deposition efficiency and easy control of composition of the deposited films.

10. Template-mediated approach

Templates such as silica and polycarbonate are used in the process. Charles R. Sides adopted polycarbon to manipulate the method as follows. An approximately 1cm^2 piece of the

polycarbonate filter is immersed in the electrode precursor solution of 1M LiFePO₄ prepared by sol-gel method in water for 24h. The impregnated template is then attached to a Pt current collector and dried in air at 80°C for 10min. The template does not require tedious etching with HF or KOH to be removed since it is decomposed into carbon just for improved conductivity. The nanocomposite electrode prepared by Charles R. Sides (C. R. Sides et al, 2005) delivers almost 100% of its theoretical discharge capacity at the high discharge rate of 3C, and 36% of its theoretical capacity at the enormous discharge rate of 65C.

Lim et al reported the mesoporous LiFeO₄ using silica (KIT-6 and SBA-15) as template which is removed finally (Sunhye Lim et al, 2008). Both the nanowire and hollow LiFePO₄ cathodes demonstrate excellent rate capability, showing 137mAh g⁻¹ at 10C rate. However such ex situ templating methods are both expensive and inefficient.

Biological systems offer capabilities for environmentally benign materials synthesis. An M13 virus-based biological toolkit has been developed for the design of nano-architected structures and materials. Yun Jung Lee fabricated high-power nanowire batteries materials using M13 bacteriophage (phage or virus) organized on a polymer surface (Yun Jung Lee et al, 2009). The gene VIII protein (pVIII), a major capsid protein of the virus, is modified to serve as a template for amorphous iron phosphate (a-FePO₄) growth. The first discharge capacity of electrode generated by this method at 10C reaches 130mAh g⁻¹. And also this nanowire LiFePO₄ shows the stable capacity retention. Cycling at 1C, up to 50 cycles, virtually no capacity fade is observed.

11. Other novel methods

Ultrasonic spray pyrolysis (USP)

An aqueous solution containing sugar and raw material is ultrasonically nebulized and a flow of argon carries the droplets through a heated tubular reactor where solvent evaporation and precursor decomposition occur. The pyrolysis product is collected in a series of water bubblers at the reactor outlet where the salt byproduct dissolves leaving LiFePO₄. The manufacturing process is one-step process and can prepare the well crystallized and homogeneous small particles with the spherical shape, pure phase. LiFePO₄ powders, reported by Mu-Rong Yang, can get the initial discharge capacity of 150mAh g⁻¹ at C/10 and 50 °C. (M. R. Yang et al, 2006)

Freeze-drying

The procedure includes four steps: preparing the precursor solution, freezing the solution, drying the congelation, and calcining the drying product. The products of freeze drying are pure amorphous nanopowder without hard agglomerations. Nanocrystals are subsequently obtained by calcination.

Coupling technique

Quantities of methods have been developed but each generated with different characteristics. The combination of two and several techniques can take the merits and discard the defects.

Microwave hydrothermal method

Compared with Hydrothermal method, the process is almost the same but only the the type of heating is changed. The mixture in water is treated in a vessel using a microwave digestion system (Maria Cristina D'Arrigo et al, 1998). Microwave-hydrothermal method can be used to crystallize nanophase materials with very high surface areas in a matter of a few minutes.

Microwave-Co. precipitation method

K. S. Park reported a capacity of 151mAh g⁻¹ of LiFePO₄ at small current density through this coupling technique (K. S. Park et al, 2003). The use of microwave greatly cut down the reaction time for Co. precipitation method so that can save the power.

Ball-milling followed by solid-state reactions

Byoungwoo Kang successfully synthesized high-rate material through ball-milling and solid-state reaction. At 50°C, corresponding to a time of 72s to fully discharge the capacity, the material achieves about 80% of its theoretical capacity (Byoungwoo Kang et al, 2009). Precursor is synthesized by ball-milling, then heating the mixture at 350°C for 10h. The sample is cooled, ground and pelletized manually then heated at 650°C for 10h under argon. The excellent rate property is thought to be caused from the strategy to facilitate transport across the surface by creating a poorly crystallized layer with high Li⁺ mobility.

Various approaches have been developed to improve electrochemical performance. In addition, the performance can be enhanced through the optimization of the synthesis processes, adjusting weight and ratio of the raw materials even with common routes. Yanyi Liu fabricated nanocomposite film cathodes by sol-gel processing with excessive polymer additive (l-ascorbic acid C₆H₈O₆) while carbon serving as both defects and conductive nanocoating on the surface of LiFePO₄ particles. High electrochemical performance with initial discharge capacity of 312mAh g⁻¹ is observed (Yanyi Liua et al, 2011). Capacities higher than theoretical limit observed in other nanostructured electrode materials have also been reported in literatures by other authors (Colm O'Dwyer et al, 2009; Chunhai Jiang et al, 2007; Dawei Liu et al, 2009). On the other hand, different carbon sources for carbon coating around LiFePO₄ particles have been implemented at enhancing the intrinsic electronic conductivity of LiFePO₄. However, many obstacles have been encountered for these methods from a laboratory process to mass production because of the complicated synthesis techniques and the hard controlled synthesis situation. The lack of an excellent large-scale synthesis technique is the obstacle to the commercial application of LiFePO₄. Therefore, it is critical to develop economic and efficient synthesis routes for the practical application of LiFePO₄ materials.

2.3 Drawback analysis

Despite the above mentioned advantages, the observed electrochemical performances of LiFePO₄ are found to be less impressive at high rates as this material has intrinsically poor ionic and electronic conductivity. A report (Amin et al, 2007) on the electronic and ionic properties of LiFePO₄ single crystals pointed out that the Li⁺ conductivity was nearly four orders of magnitude lower than the electronic conductivity along the *b*- and *c*-axes and many orders of magnitude lower along the *a*-axis, implying that mass transport of Li⁺ was crucial for improving the kinetic issues. The low ionic conductivity can be attributed to the one-dimensional nature of Li diffusion in unique olivine LiFePO₄, as clearly shown by a recent first principles calculation (Chuying Ouyang et al, 2004a, 2004b). Normally speaking, there are three kinds of possible paths for lithium ions to transport, i.e. [010], [001], [101]. Fig.5 (b) directs that three move paths, denoted as A, B and C direction, respectively. Figuring out the diffusion pathways is always crucial in understanding the microscopic diffusion mechanism. Some articles investigate the diffusion via computing with sorts of methods. Saiful Islam calculated the activation energy of various passageways to estimate the most possible transport route using well-established atomistic modeling techniques (Saiful Islam

et al, 2005). The lowest Li migration energy is found for the pathway along the [010] channel with a nonlinear, curved trajectory between adjacent Li sites. D Moran attained the diffusion constant of Li ions in different axis with density functional theory (DFT)-based calculations (D.Morgan et al, 2004) on LiMPO₄ (M Fe, Mn, Co, Ni), and have found low activation barriers for Li ion motion through one-dimensional channels. Different calculation methods lastly come into the same result as Tab.3 revealed.

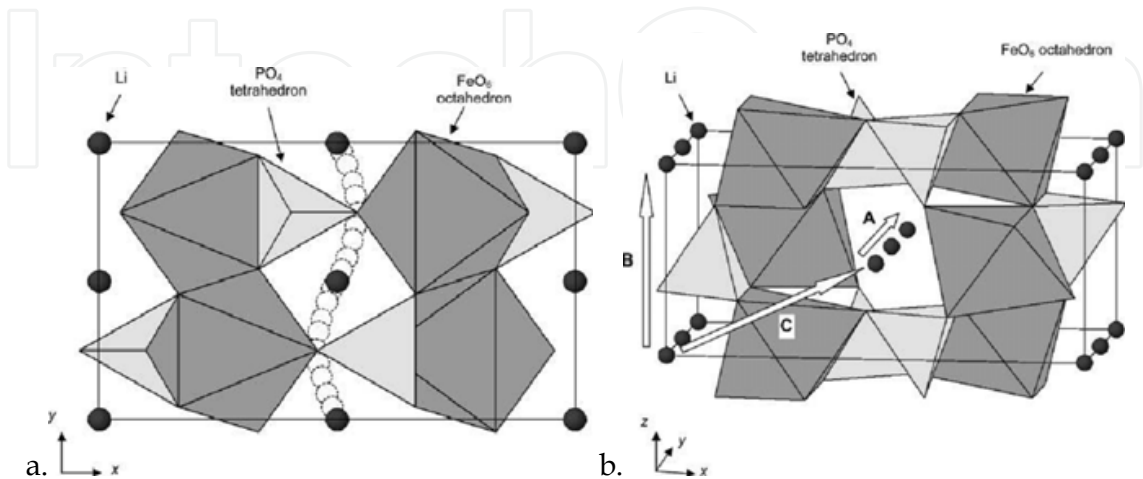


Fig. 5. Curved trajectories for Li ion migration between sites in the [010] direction. The diffusion path lies out of the *x-y* plane. (a,2D model. b,3D model, A, B, C denote [010], [001], [101] direction respectively)

This unique structure constrains the Li ions to move only in one wave-like chain since the polyhedra are slightly distorted (illustrated in Fig.5a). This “wavelike” trajectory for long-range migration results in lower migration energy than that of condition if the Li ion followed a direct, linear path. The different energy barriers for the three species are mainly due to the different atomic surroundings of the diffusion pathway, including the different ionic position and bonding length. Distortion of the *hcp* oxygen array has been related to the cation-cation coulomb repulsion across the shared edges.

	D. Morgan			M. Saiful Islam		
	[010]	[001]	[101]	[010]	[001]	[101]
Space between Li-Li	3	4.7	5.7	3.01	4.67	5.69
Emig(eV)				0.55	2.89	3.36
Eact(eV)	0.27	>2.5	1			
D(cm ² s ⁻¹)	10 ⁻⁸	10 ⁻⁴⁵	10 ⁻¹⁹			

Table 3. Description of Li⁺ migration path in LiFePO₄ crystal structure form some references

And within this crystal, all the FeO₆-octahedra can’t form a share-edge network structure because polyanions PO₄ separate them. Therefore electrons also can’t pass smoothly. In the layered compounds such as LiCoO₂, transition state of hybrid Co⁴⁺/Co³⁺ anions make a contribution to the electron conductivity between layers, whereas that don’t happen in olivine LiFePO₄ structure because FePO₄ was formed after extraction of Li⁺.

The low temperature performance of LiFePO_4 is inferior. The capacity at 0.1C (156mAh g^{-1}) and 0.3C (148mAh g^{-1}) at 25°C deteriorate largely, and only 91mAh g^{-1} and 65mAh g^{-1} are yielded at 0.1C and 0.3C at -20°C respectively.

3. Avenues to enhance performance

The performances of LiFePO_4 , however, are limited by its poor electronic conductivity and the sluggish kinetics of lithium ions to diffuse through the $\text{LiFePO}_4/\text{FePO}_4$ interface, which can result in a significant loss of capacity at high currents (Padhi et al., 1997; Prosini et al., 2002). And the high power density is the requirement of the power batteries for electric vehicles. Avenues of synthesizing composite materials, doping ions, nanocrystallization and others are introduced to clarify its improved electrochemical properties.

3.1 Composite materials

Owing to the poor inherent electronic conductivity, LiFePO_4 can be incorporated with conductive additives to form composite materials.

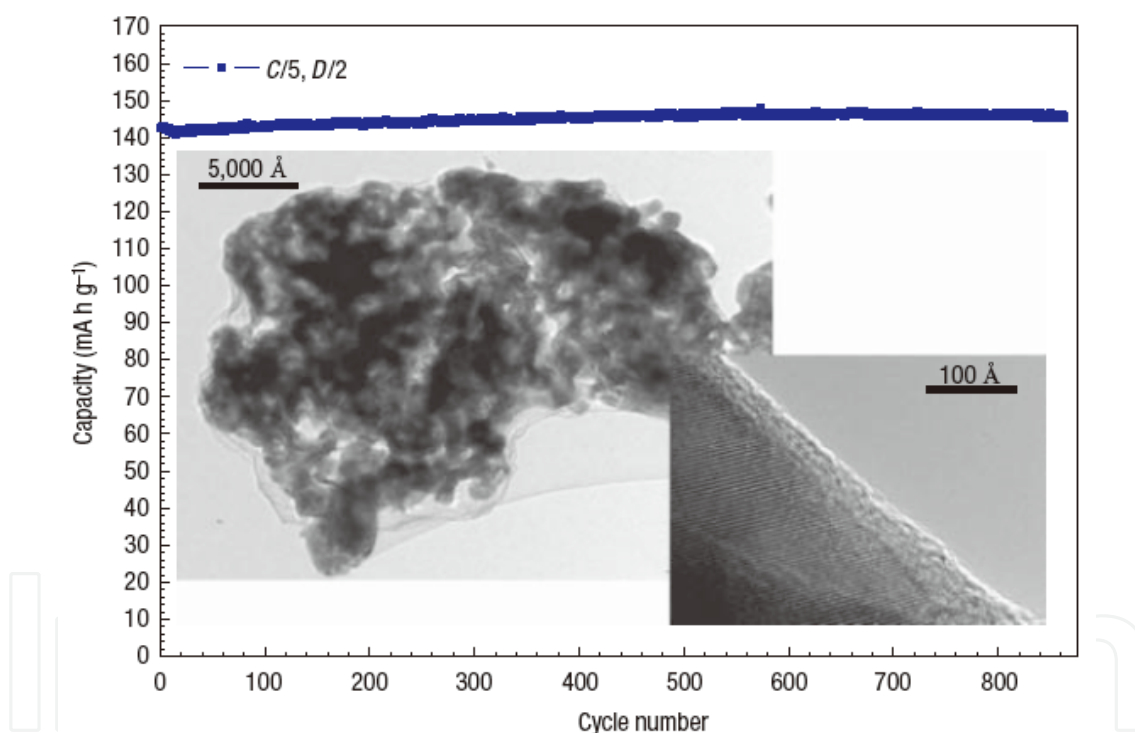


Fig. 6. The performances of C- LiFePO_4 composite materials (Aricò et al., 2005)

Carbon sources, such as acetylene black, glucose, sucrose and other organics, are added into the raw material and then carbonized at high temperature to form LiFePO_4/C materials. The LiFePO_4 particals are tightly coated with carbon and the interface between crystallized LiFePO_4 and amorphous carbon is nicely observed in Fig.6. An excellent cyclical stability is also observed. The reasons of its outstanding electrochemical performances are that the addition of carbon does not only perform its electrical conductivity, but also enhances electrolyte penetration into the cathode (Aricò et al., 2005). And the uniform small grain size would be beneficial to high rate performance. While the density of carbon is 40% lower than

that of LiFePO₄, adding too much of which would lead to low tap density and also influence volume energy density of the cathode. So a reasonable amount of it is preferred.

Electric polymer organics (PAn, PPy, PTh, PPP and so on) work with inorganic cathode has emerged as one measure to address problem. Such as adding polyaniline (PAn) into the C-LiFePO₄, both the function of electronic conductive reagents and that of active materials are performed by adding it. The capacity of 87mAhg⁻¹ can be performed by PAn at 0.1C, which can contribute to the specific capacity of the composites.

Some other materials like metals (Cu, Ag, Ni, etc.) can also be used to composite with semi-conducting LiFePO₄. TiO₂-LiFePO₄/C had higher electrochemical reactivity for lithium insertion and extraction than the un-doped LiFePO₄. The initial discharge specific capacity of the 30-min coating TiO₂-LiFePO₄/C material was about 161mAhg⁻¹, showing the potential of this material being used as a cathode material for Li-ion batteries. They decrease the charge transfer resistance and increase the surface electronic conductivity. Besides, the Fe dissolution might be simultaneously overcome by coating the LiFePO₄ particles with electrical conductive.

Compositing with additive can not only enhance the electronic conductivity and the penetration with electrolyte but also restrain the grain growth and the dissolution of Fe²⁺/Fe³⁺ ions in the electrolyte. Above all, the electrochemical performances can be improved through forming the composite materials.

3.2 Doping

LiFePO₄ is a semiconductor with a band gap of 0.3eV, which is determined by its structure. The electrons transport is restricted by the strong Fe-O bonds and the Li⁺ diffusion is limited by the Li-O bonds and one dimensional Li⁺ migration pathways. Coating LiFePO₄ with conductive materials did not change the structure parameters and had no effect on altering the inherent conductivity of the lattice, while doping ions into LiFePO₄ can make it. It could be an effective method in increasing its electronic conductivity and Li⁺ diffusion coefficient.

Many researchers have made numerous achievements. Various ions have been attempted to be doped in LiFePO₄. On the basis of different sites, it can be classified as doping at Li (M1) sites, Fe sites (M2) and O sites. Chung et al. reported chemical doping of LiFePO₄ with multivalent ions (Mg²⁺, Ti⁴⁺, Zr⁴⁺ and Nb⁵⁺) into the Li 4a site. They found the electronic conductivity was increased by eight orders of magnitude and absolute values >10⁻³ S cm⁻¹ over the temperature range from -20°C to +150°C (Fig.7). Doping it with supervalent ions can form p-type semiconductors with conductivities of ~10⁻² S cm⁻¹ arising from minority Fe³⁺ hole carriers (Chung et al., 2002).

The Li⁺ ion diffusion could be optimized by doping F⁻ into the lattice of olivine structure. The capacity is increased after doping and the value varies with the doping amount. As is shown in Fig.8, the capacities are improved after doping especially with the amount of 2%F⁻, achieving 156 mAhg⁻¹. The cycling performances are also enhanced. That could be attributed to the introduction of F⁻ into the lattice of olivine structure, which result in the weakness of Li-O bonds (Sun et al., 2010). However, as is shown above, there is an optimum doping amount to make the materials exhibit the best electrochemical performances. When the ions are doped to a certain extent, it will increase the degree of disorder of ions and so lead to the enhancement of impedance (Fig.9). And the electrochemical performances will be ultimately affected.

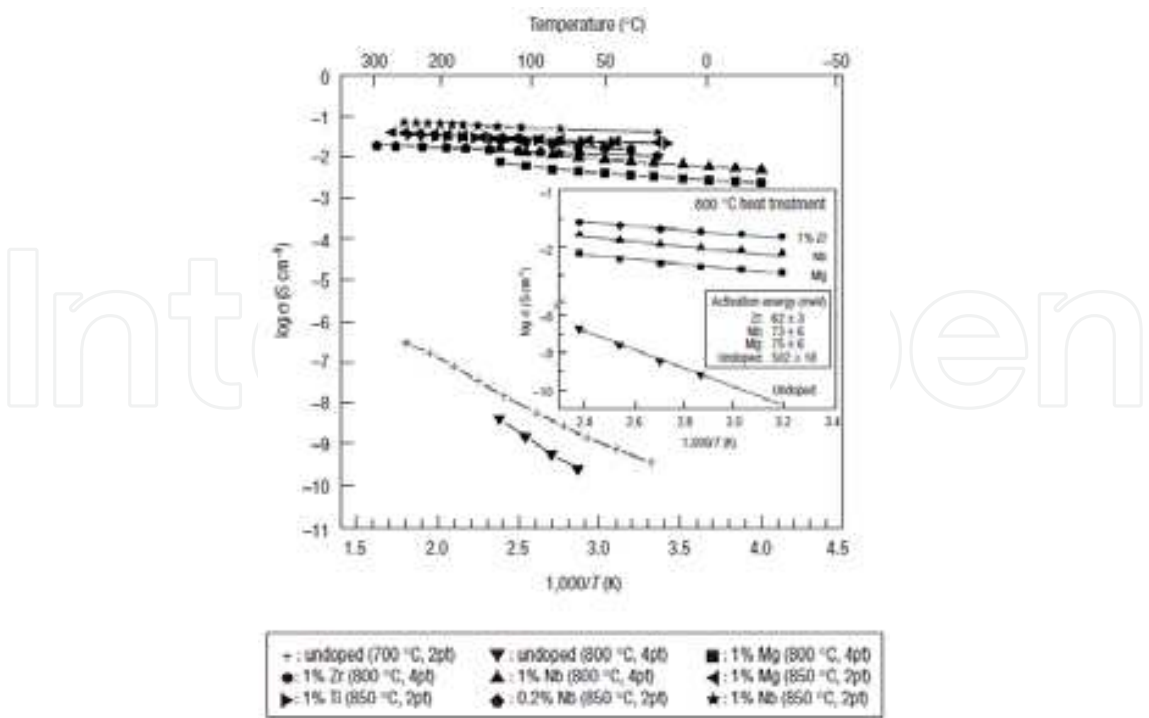


Fig. 7. The electrical conductivity of Doped olivines of stoichiometry $\text{Li}_{1-x}\text{M}_x\text{FePO}_4$ $\text{M}=\text{Mg}, \text{Ti}^{4+}, \text{Zr}^{4+}$ and Nb_5^+) (Chung et al., 2002)

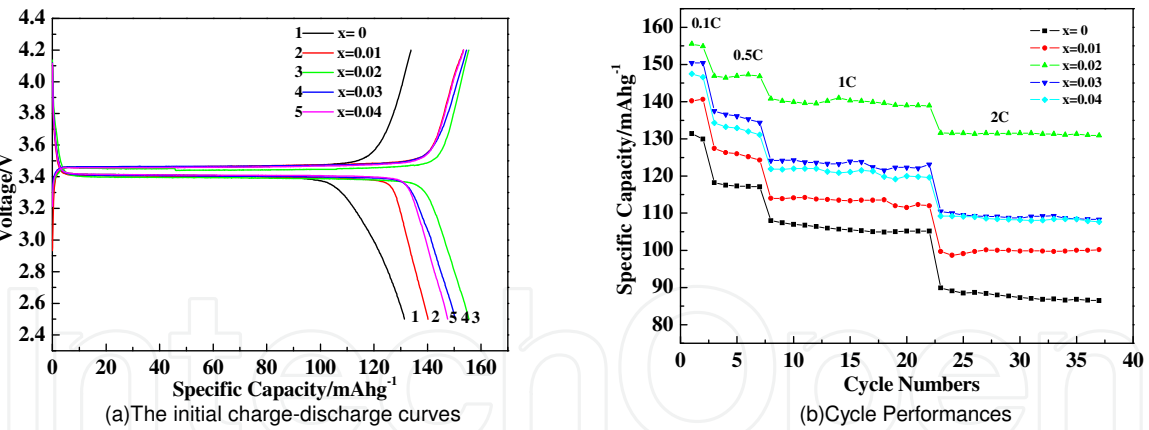


Fig. 8. The electrochemical performances of $\text{LiFe(PO}_4\text{)}_{1-x/3}\text{F}_x/\text{C}$ ($x=0, 0.01, 0.02, 0.03, 0.04$)

Compare doping with one kind of ions, the co-doping with two or more would be much more beneficial to increase the electrochemical properties. It has been proved to be successful in $\text{LiFe}_{0.99}\text{Mn}_{0.01}(\text{PO}_4)_{2.99/3}\text{F}_{0.01}/\text{C}$. Mn^{2+} and F^- addition make the lattice parameter and the cell volume expanded which can facilitate the Li^+ diffusion between LiFePO_4 phase and FePO_4 phase(Yang et al., 2010). The Mn-Cl co-doped in LiFePO_4 also shows outstanding electrochemical properties, it can be achieved the capacity of 157.7mAhg^{-1} at 0.1C and nearly unchanged after 50cycles. For all these reasons, doping is an effect avenue to enhance the inherent conductivity of the lattice.

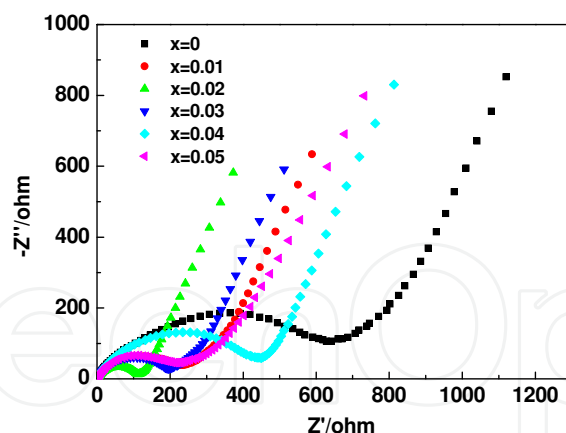


Fig. 9. Electrochemical impedance spectra of $\text{LiFe}(\text{PO}_4)_{1-x/3}\text{F}_x/\text{C}$ ($x=0, 0.01, 0.02, 0.03, 0.04$) cathodes at 25°C (amplitude is 5mV in the frequency range of $10^5\text{Hz}\sim 0.01\text{Hz}$)

3.3 Nanocrystallization and preferential growth of particles

Nanoarrays have attracted significant attention for their applications in energy storage/conversion devices. The nanocrystallization and preferential growth of cathode materials have advantages, including (i) short path length for lithium-ion and electronic transport and large surface area to enhance the electrode/electrolyte contact. All of these result in the improved cycle life and higher charge/discharge rates (Aricò et al., 2005). For the nano-sized materials, the limiting factor for charge/discharge is the delivery of Li^+ and electrons to the surface rather than bulk diffusion (Kang & Ceder, 2009). So the inferior rate performance, caused by intrinsic low diffusion, can be perfected by synthesizing the coated nano-sized materials, the ultrafast charging and discharging performances of which are remarkable to be applied on EVs (Fig.10).

The morphologies can be controlled by adopting specific synthetic routes and additive. Spherical particles, nanorods, flaky materials and nanowires are the common morphologies (Fig.11), the sizes of which are all nano level.

The lithium ions can only be extracted from LiFePO_4 and intercalated into FePO_4 in the [010] direction (Islam et al., 2005). Preferential growth of particles can shorten the (010) facet path and may increase the ratio of one-dimension tunnels in the bulk of the crystal. Hence, the diffusion across the surface towards the (010) facet can be increased to enhance rate capability.

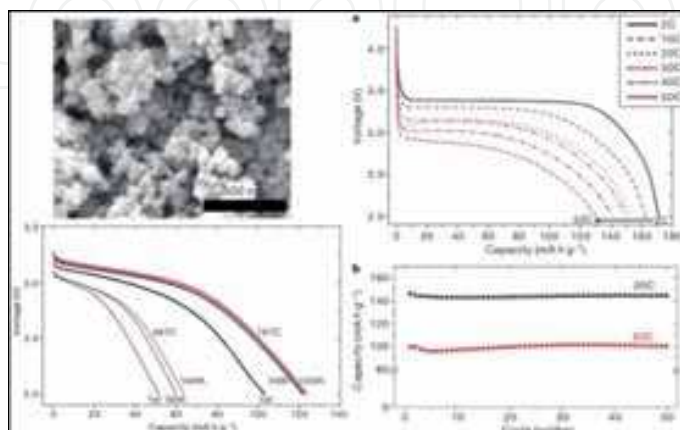


Fig. 10. The high rate performances of nano-sized LiFePO_4 . (Kang & Ceder, 2009)

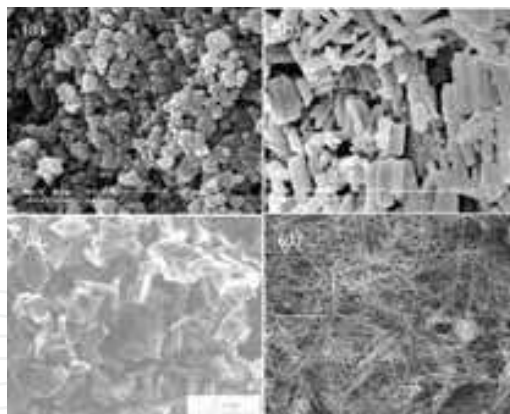


Fig. 11. The SEM micrograph of prepared LiFePO_4 with various morphologies: (a) Spherical particals(Kima et al., 2007), (b) nanorods(Huang et al., 2010), (c) flaky materials(Zhuang et al., 2005) and (d) nanowires(Wang et al., 2009)

3.4 Other means

To prepare the high power battery, the improvement of electrolyte and anode is also necessary, besides that of cathode. Especially at low temperature, the Li-ion cell containing liquid electrolyte can not cycle if the electrolyte is frozen. Ethylene carbonate (EC) is useful to form the solid electrolyte interphase (SEI) layers, but the high ratio of EC would result in high viscosity and high melting point. Adding low melting point electrolyte like Ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) would increase the Li^+ ion diffusion performance. The LiPF_6 is wildly used as electrolyte lithium salt but its weak stability leads to the formation of HF that accelerates the Fe dissolution from cathode. By contrast, LiODFB can match the low-temperature electrolyte and forms steady SEI film, so it can enhance the performances of batteries.

4. Application

To date, lithium ion batteries have become the predominant power source, owing to their high electrochemical potential *vs* Li/Li^+ , light weight, flexibility in design and superior energy density. Cost and safety are still seen as important factor limiting expansion of application of Li-ion batteries. Li-ion batteries are scattered in a wide range of industries. Mobile phone, notebook computer, and camera, such electronic products are the vast number of application. According to the need of development, Li-ion batteries tend to the use in electric vehicle.

4.1 HEV

Batteries make the consumer electronics convenient, even more after lithium ion batteries successfully enhance the power efficiency. This technology is now actively pursued for electric vehicle application. The lack of oil enhances the development of batteries, especially the one with high power and energy used in electric vehicle. High light is casted on Li-ion battery to look for hope.

Hybrid electric vehicle (HEV) is the most likely to be achieved as it combines the merits of electric vehicle (EV) and petrol-driven ones, i.e. HEV owns batteries and combustion engine simultaneously. According to the placement of combustion engine and electromotor, HEV is

divided into series-type and parallel-type. S-type HEV is driven by batteries which are charged by combustion engine. P-type HEV uses electromotor to work during complicated and changeable working condition (launch, speed change, et al), and it shifts to combustion engine if condition is steady such as long-distant course in suburb. Both P and S-type avoid the loadswing and fast response of combustion engine whereas the fuel automobiles do which can lessen thermal efficiency. Related to mass application in HEV, the most appropriate power system should be splendid in terms of safety, cycle, calendar lifetime and cost. In addition, the availability and cost of the transition metals used in these compounds are unfavorable as the Wh/\$ is a more important figure of merit than Wh/g in the case of large batteries to be used in an electric vehicle or a load-leveling system. Batteries are not so demanding in high energy and also capacity could not be high since engine can charge it consecutive. In HEV systems the operation windows would be defined much smaller (e.g. SOC=30–60%), according to power requirements, cold cranking and aging issues.

Low cost, long cycle life and non-toxic are the most obvious advantages of LiFePO₄. It's normal for LiFePO₄ to maintain almost sound structure after 1200 cycles at 1C. The power capability of olivine cells for very short-term pulse durations is nearly independent from SOC and SOC history. As a reference, the current price per unit of LiFePO₄ ranges from \$1.90/Wh to \$2.40/Wh. Although a little higher compared with \$0.86/Wh for typical manganese-based Li-ion batteries, it is estimated that the price of LiFePO₄ will go down accompanying with the rapid development of technique. It is reported that the electrolyte decomposes completely below the limit of 5.0V with lithium cobalt and manganese oxides as cathodes due to the catalyses effects on the electrolyte/electrode interface. The overcharge test of LiFePO₄ doping with Al³⁺ appreciates a higher electrolyte decomposing voltage plateau that appeared between 5.20 and 5.45V (Hui Xie et al, 2006). It has been proved that LiFePO₄ can maintain the perfect olivine structure of the composite under overcharging conditions. Its thermal stability is superior as LiFePO₄ can endure condition under 400~500°C (~200°C for LiCoO₂ and LiMn₂O₄). LiFePO₄ as cathode material has become one of the most promising candidate for hybrid/electric vehicle propulsion.

4.2 Potential in future

LiFePO₄ is adaptable to serve as the safety motive power so can scatter in much more fields besides vehicle. The prospect of the design of the rubber-tyred container gantry crane without diesel generating set becomes more and more practical owing to the application of this new energy storage unit. The transfer of the rubber-tyred gantry crane can be solved in essence owing to the adoption of lithium iron phosphate battery to supply power. Based on the development trend of the substation system, i.e. high-degree of automation and integration of service supply, the ferric phosphate lithium cell accelerates the step of bringing the trend into practice. It also can enhance the usage efficiency of green energy resource (solar, wind, et al) aiming at address the instability problem of these system since electricity produced by solar and wind are not always constant. LiFePO₄ has attracted considerable attention as next generation cathode material of lithium ion battery.

5. Conclusion

More knowledge is understood about LiFePO₄ and much more rapid is the ongoing progress. Lithium ion batteries have become the predominant power source, owing to their

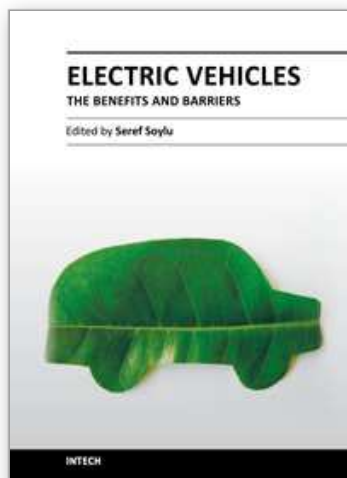
high electrochemical potential *vs* Li/Li⁺, light weight, flexibility in design and superior energy density. To date, quantities of methods have been developed in order to realize mass practical application with favorable properties. Avenues of synthesizing composite materials, doping ions, nanocrystallization and others have been conducted to improve electrochemical properties. More enterprises dedicate their efforts into manufacturing olivine cell besides A123, Valence in USA and Phostech in Canada, the industry giants related to LiFePO₄ material. Quantity production and mass application are much closer to reality due to the durability, non-toxic, high capacity and energy density of LiFePO₄. The iron based olivine type cathodes (mainly lithium iron phosphate, LiFePO₄) are regarded as possible alternatives to cathodes based on rare metal composites.

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In this book, theoretical basis and design guidelines for electric vehicles have been emphasized chapter by chapter with valuable contribution of many researchers who work on both technical and regulatory sides of the field. Multidisciplinary research results from electrical engineering, chemical engineering and mechanical engineering were examined and merged together to make this book a guide for industry, academia and policy maker.

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