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REVIEW

Developments of lithium-ion batteries and challenges of $LiFePO_4$ as one promising cathode material

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Abstract Developments and developing trends of lithium-ion batteries (LIBs) are summarized first: it is proposed that solid thin film microbatteries and large-scale all-solid-state rechargeable LIBs are the two main developing tendencies. Meanwhile, cost and safety issues are the primary limitations to improve advanced LIBs with excellent electrochemical performance. Next, one of the most promising cathode materials, $LiFePO_4$, is introduced in detail. Advantages and drawbacks of $LiFePO_4$ as cathode active material are analyzed, then, main approaches to circumvent its drawbacks proposed by many groups are also summarized. In addition, some mechanism investigations on this cathode material presently and challenging problems waiting for solutions before $LiFePO_4$ can be commercialized are also discussed in this review.

Developments and developing trends of Lithium-ion batteries

Since $LiCoO_2$/C rocking chair cells were commercialized by Sony Corporation in 1991, rechargeable Lithium-ion batteries (LIBs) have become very important components in portable, entertainment, computing, and telecommunication devices required by modern information-rich, mobile society, such as camcorders, MP4-players, lap tops and cellular phones. Lithium-ion batteries are presently manufactured at a rate of several millions of units per month, mostly by Japanese manufacturers [1], and production of LIBs is expanding continuously in line with increasing demand from the electronic industry.

Lithium-ion batteries $LiCoO_2$/C are widely used in most of modern high-performance portable electronic devices. This type of rechargeable LIBs has a potential over 3.6 V, which is three times that of alkaline systems. In addition, their gravimetric energy densities as high as 120–150 W h kg^{-1} are about two or three times those of Ni–Cd batteries [2], and this advantage of LIBs is primarily important for hand-held devices, but it is not a concern for most power or storage applications. Although a lot of achievements have been attained since the International Power Source Symposium (IPSS) in Manchester in 2001, the major development in rechargeable lithium batteries is the replacement of lithium cobalt oxide with lithium cobalt/nickel oxide as the cathode material [3]. Active investigations are continuing in all aspects (anodes, electrolytes, cathodes, construction, and so on) of batteries to further improve characteristics such as energy density, rate capacity, cycleability, life expectancy, stability, etc., and various kinds of new anode, electrolyte, and cathode materials with higher performance than the conventional ones have been discovered vigorously [4].

In addition to numerous applications in modern electronic devices, there are other promising developing trends of LIBs. One of them is thin film lithium-ion microbatteries, which have been developing for several years [5–10]. Thin film Li-ion microbatteries can be used as an integral part of miro-electronic circuits (on-chip CMOS memory backup) or miniature hearing aids and implanted medical devices [6]. Thin film electrodes and solid thin film electrolytes are indispensable, which will be discussed in the following parts concerning electrode and electrolyte materials.

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Another trend is large-scale Li-ion batteries [11–14], which have been developed for energy-saving systems such as home-use load-leveling systems, stationary backup systems, hybrid electric vehicles (HEVs), and electric vehicles (EVs) [12]. The low cost, safety, environmental benignity, and long cycling life of LIBs are attractive features for the application of large-scale LIBs. Cobalt oxide-based materials are unsafe and are environmentally toxic. Therefore, new active materials that meet these requirements must be found [11, 15].

However, there are two major problems limiting much wider applications of LIBs, namely, cost and safety [3, 8], and these were raised at the 23rd IPSS in Amsterdam in September 2003. Eighty percent of the cost of LIBs is the cost of materials. In addition, the voltage needs to be controlled and cannot exceed 4.6 V for safety [3], since LIBs usually contain flammable organic electrolytes, which under certain conditions (for example, uncontrolled charging above 4.6 V), may provoke smoke and fire.

In order to decrease the cost of lithium batteries, main efforts are devoted to the reduction of the costs of the active electrode materials. To solve the cost problem seems to be especially urgent for the practical applications of large-scale LIBs, where a large amount of active materials are consumed. Consequently, conventional costly cobalt oxide-based materials will likely be replaced with lower-cost materials such as those containing iron and manganese, which are naturally occurring [15].

Apart from cost, solid-state lithium batteries have been regarded as a fundamental solution to the safety concerns raised by conventional LIBs employing nonaqueous electrolytes [16]. Presently, solid-state lithium batteries have attracted a great deal of attention due to their potential superior characteristics in comparison with conventional LIBs [7, 16, 17]. Thereinto, rechargeable thin film LIBs are one typical type of solid-state lithium batteries, which also can be fabricated into Li-ion microbatteries. All-solid-state LIBs, meaning that electrode and electrolyte materials are all solid and leak proof, exhibit high safety performance, are mechanically robust and can be operated over a wide range of temperature.

One of the most promising cathode materials $LiFePO_4$ for the next generation LIBs

Cathodes are very indispensable and key part of LIBs, and cathode materials are devoted much efforts in order to decrease costs and to circumvent safety issues. Good cathode materials have to meet the following criteria: high capacity that can be retained for up to 1000 cycles; stability that can endure high-rate recharge and discharge and other possible extreme conditions; affordability for consumer electronics and large-scale storage, and low toxicity [18]. Though $LiCoO_2$ is the dominant cathode material at present in the LIBs industrial world, alternative materials for cathodes have been developed including $LiNiO_2$, $LiMn_2O_4$, and other novel compounds [4]. $LiNiO_2$ exhibits good specific capacity in comparison with $LiCoO_2$, but because of safety concerns after exothermic oxidation of the organic electrolyte with the collapsing delithiated Li_xNiO_2 structure [2], pure $LiNiO_2$ is not commercialized solely. Delithiated Li_xCoO_2 was found to be more thermally stable than Li_xNiO_2. In order to overcome drawbacks of both materials and keep their merits, substitution of Co for Ni in Li $Ni_{1-x}Co_xO_2$ was adopted to alleviate safety concerns resulting from $LiNiO_2$. The advantages are that nickel is cheaper than cobalt, and that a higher capacity (180 mAh, cf. 127 mAh) can be achieved because only 1/2 of the lithium reacts in the pure lithium cobalt oxide, while 2/3 of the lithium can react in the mixed lithium nickel/cobalt oxide [3]. To circumvent safety and capacity issues, several routes have been investigated: using inert di-, tri-, or tetravalent cationic substitute for Ni or Co(Al, Ga, Mg, Or Ti); $Li_xMnO_4 \rightarrow Li_{1+x}Mn_{0.5}Cr_{0.5}O_2$, unfortunately Cr is toxic and costly. Furthermore, nanostructured $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode is prepared by PLD in oxygen environment [17]. Al doping increases thermal stability of these films and decreases particle size. Consequently the ion diffusion pathways in grains are diminished and the rate capability of the cathode is therefore improved.

The spinel $LiMn_2O_4$ is regarded as a promising 'green' 4 V cathode material in rechargeable LIBs, because it is naturally abundant, environmentally friendly and has good safety characteristics, although it possesses 10% (110 mA h g^{-1}) less capacity than $LiCoO_2$ [3]. Lithium ions are reversibly inserted into and extracted out of the host cubic spinel phase in two composition ranges, $0 \leq x \leq 1$ and $1 \leq x \leq 2$, which produce two-voltage plateaus at 4 and 3 V, respectively [19–21]. However, one serious drawback of spinel $LiMn_2O_4$ is the significant capacity fading during cycling at elevated temperatures (≥55 °C). Capacity fade in $LiMn_2O_4$ are of two kinds: reversible capacity loss and irreversible capacity loss. The reversible capacity loss results from the low mobility and hence long diffusion path lengths for Li-ion transport in the lithium manganese oxide crystallites. Reversible capacity loss usually can be minimized at smaller currents and over a larger discharge time. Irreversible capacity loss is related to [22, 23]: (i) electrolyte decomposition at high potentials; (ii) slow dissolution of $LiMn_2O_4$ through the reaction: $2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$; (iii) irreversible structural transition at the discharged state; and (iv) transformation of the unstable two phase structure in the higher potential region to a more stable single-phase structure via loss of MnO.

Great efforts have been devoted to overcome these drawbacks of $LiMn_2O_4$, and many approaches such as doping, surface coating, rich-lithium method, and morphology modification have been adopted to enhance its cycleability, capacity, and rate capability. For an instance, partial replacement of Mn in $LiMn_2O_4$ by some low valent metal ions such as, Ni^{2+}, Al^{3+}, and Cr^{3+} can effectively enhance its cycleability [24, 25]. Surface coating of the spinel to avoid Mn dissolution is an effective method to reduce capacity fades of $LiMn_2O_4$ [26, 27]. The capacity retention of a $Li_{1+x}Mn_{2-x}O_4$ spinel-based cell is improved compared with stoichiometric $LiMn_2O_4$, because of the excess of lithium protects the Li–Mn-oxide spinels against Jahn-Teller distortion, but decease the capacity of the electrode material due to substitution of Mn^{3+} ions in octahedral sites [28, 29]. Nanostructured $LiMn_2O_4$ with various morphologies have been expensively prepared to improve their rate capability, such as nanoparticles [30], nanowires [31], and hollow nanosphere [32], but such an improvement is often considered to be achieved at the expense of high volumetric energy density. Recently, it has been reported that a small amount of fluorine substitution for oxygen can reduce Ni and Mn dissolution from HF attack, enhancing the electrochemical properties and thermal stability [33]. In [34], fluorine-doped 5 V cathode materials $LiNi_{0.5}Mn_{1.5}O_{4-x}F_x$ were prepared by sol–gel and postannealing treatment method, and electrochemical performances of samples indicated that stable cycleability can be obtained when the fluorine amount x is higher than 0.1, but the specific capacity is decreased. In general, trying to low synthesis cost, to circumvent safety issue, and to realize the improvement of electrochemical behaviors (such as cycleability and rate capability) but without expenses of initial capacity, high volumetric energy density are still investigation interests of $LiMn_2O_4$ researchers presently.

Recently, NASICON or olivine polyoxyanion structures, built from MO_6 octahedra(where M is Fe, Ti, V, or Nb) and $XO_4{}^{n-}$ (where S, P, W, or Mo) tetrahedral anions, have been discovered as cathode materials, but one drawback of these materials is their poor intrinsic electronic conductivity. This kinetic limitation had to be overcome through various materials fabrication approaches, including carbon coating, minimization of particle size, or doping. In addition, since the energy density of conventional $LiCoO_2$/graphite is reaching the technological limits [4], new requirements for large-scale LIBs and thin film lithium batteries applications call for new materials. The phospho-olivine-type $LiFePO_4$ or variants with other transition metals are promising candidates for cathode materials, which are likely to meet many of the demands intrinsic to the next generation LIBs [18]. In this section, lithium ion phosphate $LiFePO_4$ with olivine polyoxyanion structure, one of the most promising cathode materials for next generation LIBs, will be introduced in detail.

Advantages and drawbacks of $LiFePO_4$

$LiFePO_4$ has recently attracted considerable attention since it was first proposed by Padhi et al. [35], because of its potential application as the next generation cathode material in LIBs. Compared with conventional cathode materials $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$, $LiFePO_4$ has many advantages such as appreciable theoretical capacity (ca. 170 mA h g^{-1}), moderate operating flat voltage (the Fe^{3+}/Fe^{2+} redox couple is conveniently located at 3.4 V versus Li+/Li, which is compatible with common organic, as well as polymer electrolytes [36], corresponding to the theoretical energy density 580 W h kg^{-1} versus Li+/Li, then above the value of $LiCoO_2$ [37]), thermal stability, excellent reversibility, low cost, environmental benignity.

Phospho-olivine-type $LiFePO_4$ (Fig. 1) has an orthorhombic unit cell (D_{2h}^{16}-space group *Pmnb*) [35], which accommodates four units of $LiFePO_4$, and the oxygen ions form a hexagonal close-packed arrangement. The metal Fe ions form zigzag chains of octahedrons in alternate basal planes bridged by the tetrahedral phosphate groups (PO_4). The lithium atoms occupy the octahedral sites, which are located in the remaining basal planes, and Li^+ ions form one-dimensional tunnels in the structure that run parallel to the planes of corner-sharing FeO_6 octahedra, along the [010] direction in the orthorhombic *Pmnb* lattice. The strong covalent bonding between the oxygen and P^{5+} ions forming $(PO_4)^{3-}$ units allows for the greater stabilization of the structure compared with layered oxides such as $LiCoO_2$, $LiNiO_2$, and $LiMn_2O_4$, in which the oxide layers are more weakly bound [35]. This strong covalence stabilizes the antibonding Fe^{3+}/Fe^{2+} state through a Fe–O–P inductive effect. Consequently, oxygen atoms are a lot harder to extract [38]. With this kind of three-dimensional framework, $LiFePO_4$ shows high thermal stability at high temperature.

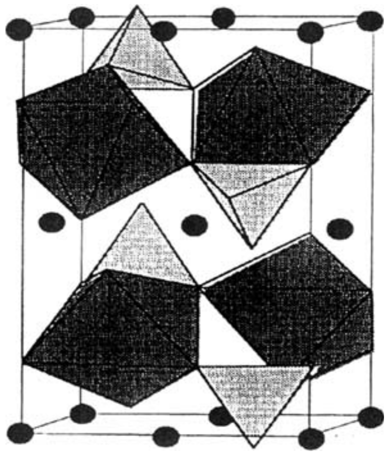

Fig. 1 Structure of $LiFePO_4$, illustrating the position of Li atoms (*small spheres*) in the unit cell. Small tetrahedral PO_4 and FeO_6 octahedra

This guarantees stable operation at higher temperatures and safety under abusive conditions, adding greatly to the attractiveness of $LiFePO_4$ [39]; the P_{tet}–O–Fe_{oct} linkage in the structure generates a suitable Fe^{3+}/Fe^{2+} redox energy of flat voltage 3.4 V versus Li/Li^+ [40]. Excellent cycling reversibility is due to the fact that $LiFePO_4$ and $FePO_4$ are isostructural (space group *Pnma*) with only a slight difference in the cell parameters: the volume decreases by 6.81% and the density increases by 2.59% when $LiFePO_4$ delithiated into $FePO_4$ [35]. Furthermore, $LiFePO_4$ triphylite is a naturally occurring mineral, which is abundant in nature. Consequently, with $LiFePO_4$ as cathode materials, the cost of LIBs will be reduced greatly. It has been estimated that use of lithium iron phosphate as cathode material could reduce the cathode cost from 10% to 50% of the battery cost [8]. The transition metal employed in $LiFePO_4$, Fe, is nontoxic unlike nickel and cobalt, which are used in current LIBs [3], hence a better environmental friendliness. Therefore, this promising cathode candidate is perceived as being ‘green’ too. In addition, vacant interstitial sites available in the structure provide the Li^+ ions with more freedom to migrate, and it is electrochemically proven that Li^+ ions can be reversibly inserted into and extracted from the interstitial sites [41].

However, it should be noted that there are three intrinsic negative aspects of olivine-type materials for LIBs: (1) the much lower intrinsic electronic conductivity of $<10^{-9}$ S/cm in $LiFePO_4$ which prevents full use of its theoretical capacity [42], particularly in the Mn-rich phase [43]. Carrier (mobile electron polaron or hole polaron) density in the monovalent stoichiometric end members should be negligible, and this evidently accounts for the very low electronic conductivity of $<10^{-9}$ S/cm in $LiFePO_4$ [44]. It is also likely that the low conductivity is related to the FeO_6 linking (corner-sharing rather than edge- or face sharing) and the large separation between Fe atoms [45]; (2) the lower true volumetric density ($LiMnPO_4$: 3.4 g/cm^3; $LiFePO_4$: 3.6 g/cm^3; $LiMn_2O_4$: 4.2 g/cm^3, $LiNiO_2$: 4.8 g/cm^3; $LiCoO_2$: 5.1 g/cm^3) [39, 46]; and (3) low Li-ion diffusion coefficient. The chemical diffusion coefficients were found to be in the range of 10^{-11} to 10^{-13} cm^2 s^{-1} depending on the Li concentration and on the characterization method used [47]. These three intrinsic drawbacks of $LiFePO_4$ pose a bottleneck for the commercial applications [46]. In addition, reversible capacity loss at high current density is another fatal shortcoming of $LiFePO_4$. This poor performance is regarded as the direct consequence of polarization arising upon cycling at high current density [35, 36, 45, 48].

Approaches to improve the electrochemical performance of $LiFePO_4$

In recent years, considerable efforts have been devoted to circumvent the drawbacks mentioned above. Various synthesis routes such as co-precipitation [49], hydrothermal routes [18, 50, 51], mechanochemical activation method [52], pulsed laser deposition [53–55], and ultrasonic spray pyrolysis [46] have been proposed to prepare $LiFePO_4$ [56]. The most common and traditional method to fabricate $LiFePO_4$ is still solid-state reaction synthesis [48, 57], which required a lengthy firing at 300-800 °C. Unlike the conventional heating, microwave heating introduced by Higuchi et al. to the preparation of $LiFePO_4$ cathode material [58], is a self-heating process that occurs through the absorption of electromagnetic energy, and the microwave energy is directly absorbed by the sample. Uniform and rapid heating can be achieved with a short period of time and at temperatures lower than that required for furnace heating. Therefore, microwave heating method is expected to be an economical and convenient synthesis approach of $LiFePO_4$ ceramic powders with homogeneous microstructures and fine grain size [58–60]. In order to overcome the above drawbacks of $LiFePO_4$, all these different fabrication approaches can be generally divided into three categories. In other words, there are generally three approaches to improve the electrochemical performance of $LiFePO_4$: (1) to enhance the electronic conductivity by introducing conductive addictives, i.e., coating carbon through the synthesis of $LiFePO_4$/C composite [40, 48, 50, 52, 61–65], or dispersing copper, silver, etc., into the solution during synthesis [45]; (2) to control the particle size and grow homogeneous polycrystalline $LiFePO_4$ nanoparticles by optimizing the synthesis conditions [38, 66]; and (3) to selectively dope with cations supervalent to Li^+ [41, 45]. Croce et al. improved the kinetic properties of $LiFePO_4$ by dispersing copper or silver into the solution during synthesis, and the finely dispersed metal powder promoted a reduction of particle size and an increase in the material conductivity [67]. The improvement of the electrochemical performance of $LiFePO_4$ by different approaches will be reviewed as follows.

Carbon coating

The carbon-coating strategy was initially proposed by Armand and co-workers, who reported an improvement in the kinetics of the electrochemical reaction after carbon coating [68]. This leads to practical-specific capacities approaching the theoretical value of 170 mA h g^{-1} for the pure material at room temperature. In general, there are four important functions of carbon coating [40]: (1) to act as a reducing agent to avoid formation of trivalent Fe ions during fabrication; (2) to maintain the particles isolated from each other preventing the consequent undesirable particle growth; and (3) to enhance the intra- and interparticle electronic conductivity; (4) to avoid the aggregation of nanoparticles and to provide passages for lithium ions [65].

It was confirmed that conductive carbon had to be homogeneously dispersed in the cathode in order to promote electronic conductivity and particle connection [53]. It was found that the lithium-ion diffusion coefficient in the nanocomposites was affected by the incorporated carbon, and markedly increased with the carbon content [69]. The carbothermal effects on the purity of phases by using magnetic experiments when synthesizing $LiFePO_4$ were investigated and results indicated that addition of 5% carbon withdrew traces of the Fe(III) phase such as Fe_2P and/or Fe_2O_3 [61]. In [63], three different carbon conductivity additives (vapor-grown carbon fibers (CF), carbon black (CB), and graphite (GR)) were used in order to compare their coating efficiencies. The results demonstrate that cathodes containing CF + CB have the best power performance, followed by cathodes containing CF only and CB + GR. An electrodeposited C-$LiFePO_4$/conductive polymer PPy composite cathode exhibits a significant enhancement of the capacity and rate capacity of LIBS [62]. A high capacity and stable cycling was retained at a 10C charge rate. Improvement in electrochemical performance has been also achieved by using poly(vinyl alcohol) as the carbon sources for the as-prepared materials [40].

A dense electrode with a minimum amount of carbon is required for a higher volumetric and gravimetric energy density of LIBs. However, carbon coating causes a reduction in the volumetric energy density of the electrode [45]. Therefore, it is necessary to optimize the carbon content in $LiFePO_4$ during the carbon-coating process.

In order to improve the electronic conductivity, the key point of carbon-coating methods is to find the most suitable carbonaceous material or a combination of materials, and to find simpler, cheaper, and more efficient fabrication procedures.

Minimization of particle size

The observed capacity loss of LIBs upon cycling is known to result from the utilization of large particles constrained by their small surface area and from the diffusion limit of lithium ions through the decreasing $LiFePO_4/FePO_4$ interfaces, as described by Padhi et al. [35, 38]. It was also found that the rate capability of $LiFePO_4$ is mainly controlled by its specific surface area [11, 50]. Consequently, an effective way to improve the rate capability of $LiFePO_4$ cathode is to minimize particle size and increase its specific surface area. As-prepared $LiFePO_4$ in [11] has a high-specific surface area of 24.1 $m^2\ g^{-1}$, an excellent rate capacity and can deliver 115 $mA\ h\ g^{-1}$ of reversible capacity even at a 5C rate.

The benefit of having a nanostructured material is obvious, particularly when high rates of charge-discharge are used. The finer the particles, the better the electrochemical performance [37]. Fine and homogeneous nanoparticles of $LiFePO_4$ with high crystallinity were produced by using poly-ol process [38]. Supercritical hydrothermal synthesis is promising as an effective method of obtaining fine particles of $LiFePO_4$ with high crystallinity [66]. Results demonstrate that the purity of the particles was affected mostly by pH values, whereas the size and morphology were affected mostly by temperature.

The use of nanoparticles in composite electrodes may have considerable kinetic advantages because of the reduction of the diffusion pathway length of Li^+ in the electrode materials, and also because of the reduction of the overall charge-transfer resistance of the electrodes [70]. Therefore, reducing the particle size is expected to act on the ionic conductivity owing to the reduction of the diffusion length of the lithium ions in the solid nanocrystalline particles. In contrast, adding a carbon coating should mainly affect the electronic conductivity [71].

The particle size of $LiFePO_4$ decreases as the carbon content increases during carbon coating. $LiFePO_4$ with medium carbon contents have a small charge-transfer resistance and thus exhibit superior electrochemical performance [40]. However, as mentioned above, carbon coating can improve the conductivity of active materials, but will decrease the volumetric energy density. Therefore, it is important to balance the improvement of electrochemical performance and the reduction of volumetric density.

Doping with cations supervalent to Li^+

Chung and co-workers found that low-level doping with supervalent ions(for example, Mg^{2+}, AL^{3+}, Ti^{4+}, Zr^{4+}, and Nb^{5+}) into the Li 4a site increased the electronic conductivity by a factor greater than 10^8, by the introduction of p-type and n-type conductivity at the fully discharged and charged state, respectively [72]. It was also found that the bulk conductivity of the olivine was improved by a partial substitution of Fe^{2+} with Mn^{2+} resulting in large-specific capacity (>140 $mA\ h\ g^{-1}$) and small capacity fading [45]. Nb doping also improved the electronic conductivity of the composite significantly, decreased the resistance and polarization, and enhanced the reversible capacity remarkably at high-charge/discharge rates [48].

It was demonstrated that polarization, especially in deeply charged and discharged states, grew considerably with cycling, which implied that the electronic and/or ionic conduction was not fast enough in $LiFePO_4$. Fortunately, it was shown that cation substitution could result in an enhancement of the high current rate performance of LIBs as well as a reduction of polarization [45]. These results implied that the electronic conduction was enhanced so that the kinetic limitation on the electrochemical redox reaction was somewhat relaxed. This is another possible approach to overcome the kinetic limitation. Another important aspect of this result is the possibility to reduce the carbon content of the $LiFePO_4$-based cathode material in order to increase the volumetric energy density.

However, some arguments favor the doping effect as the relevant influence on the conductivity increase by a modification of the electronic structure of $LiFePO_4$. Other arguments favor low-valence iron derivative as responsible for the high conductivity in these compounds rather than the doping effect [73]. Our research group had tried to dope $LiFePO_4$ thin films with supervalent ions Ti^{4+}, Zr^{4+}, Nb^{5+} by pulsed laser deposition, but unfortunately, obtained $LiFePO_4$ thin-film doped with these supervalent ions cannot be realized the conductivity improvement. In general, the doping effect on the conductivity of $LiFePO_4$ is a controversial issue unresolved presently, and the exact mechanism for the increased electronic conductivity is still a subject of research.

In summary, in order to overcome these kinetic limitations, optimized $LiFePO_4$ electrodes should be fabricated through a combination of several approaches [74]. For example, with highly improved electrochemical performance, $Li_{1-5x}Nb_xFePO_4/C$ composite electrodes were synthesized by a one-step solid-state reaction, which resulted from the combination of the carbon-coating and doping approaches [48].

Mechanism research concerning $LiFePO_4$

In keeping with the pace of the synthesis development of $LiFePO_4$, numerous mechanistic studies have been conducted in order to understand the fundamental properties of $LiFePO_4$ as a cathode material, such as explaining the capacity fade mechanism at high current density or dealing with its two-phase nature (one phase lithitated LiFePO4 and the other delithiated $FePO_4$).

Various mechanisms have been proposed to explain the capacity fade or poor-rate capability occurring in LIBs, most of which point out the stability of one or both electrodes: (1) increase in impedance over time [26, 48, 53, 69]; (2) loss of lithium due to solid-electrolyte interface (SEI) layer build up [3, 7, 15, 75]; (3) degradation of the cathode [4, 35]; (4) loss of carbon as conductive additive from cathode [76]; (5) utilization of large particles constrained by their small surface area and the diffusion limit of $Li+$ through the decreasing $LiFePO_4/FePO_4$ interface [35, 38]; (6) polarization effect upon cycling at high charge/discharge rate because of poor electronic and/or ionic conductivity [35, 36, 45, 48].

Padhi and co-workers first explained the poorer-rate capacity under high-charge rate by using a two-phase shrinking-core model [35]. Their experimental results demonstrate that the voltage $V(x)$ for $Li_{1-x}FePO_4$ is independent of x over a large range of x. By Gibb's phase rule, this implies that the extraction/insertion reactions proceed by the motion of a two-phase interface. As it is well known, the most obvious difference between the two-phase system and solid-solution system (single-phase) is different equilibrium potential characteristics, that is, the equilibrium potential of a single-phase system is composition-dependent, whereas that of a two-phase system is constant over the entire composition range [77]. Consequently, the model for lithium extraction/insertion in $LiFePO_4$ is generally adopted as a two-phase process. Most researchers have used this two-phase model to explain their experimental phenomena [37, 40, 45, 64, 77–79]. The phase diagram for Li_xFePO_4 has been determined for different lithium concentrations and temperatures. The mixing transformation from the heterosite and triphylite phases to a disordered solid solution of Li_xFePO_4 occurs around 200 °C. The heat of transformation was measured for an $x = 0.5$ sample, and was estimated to be at least 700 J/mol [80]. However, Lemos and co-workers recently questioned the two-phase model because they found that in the case of the $Li_{0.11}FePO_4$ oxide, the spectra cannot be reproduced just by the superposition of the end member profiles. An additional broadband contribution was found in both Raman and infrared spectra probably due to a disordered structure present in the mixture, which implied that the well-accepted two-phase model for the delithiation process in $LiFePO_4$ was incorrect. Therefore, they suggested revising the two-phase model by including the new phase they detected for a particular level of lithium extraction close to that of complete oxidation of the Fe^{2+} ions to Fe^{3+}. Yamada et al. [81] with their Rietveld refining of X-ray data also suggested that these solid solutions could also exist at room temperature as narrow end member at the high and low lithiation limits. However, Delmas et al. reported their newest research progress and proposed a 'domino-cascade model' to describe the lithium deintercalation/intercalation mechanism [82]. Their X-ray diffraction and electro microscopy results show the coexistence of fully intercalated and fully deintercalated individual particles, and structural constraints occur just at the reaction interface. The 'domino-cascade model' is in good agreement with the EELS study reported by Laffont et.al. [83], which showed that there is no solid solution in the interfacial region between the two limit compositions. More recently, Gibot et al reported the feasibility to drive the well-established two-phase room-temperature insertion process in $LiFePO_4$ cathodes into a single-phase one by modifying the material's size and ion ordering [84]. Their results set up new challenges, as downsizing a particle can affect both structure and composition.

There are many other investigations on $LiFePO_4$. Structural and magnetic properties of lithium extraction effects have been investigated in [85], and some results show that magnetic clustering occurs during the preparation process of $LiFePO_4$. The magnetic clusters are nanometer-sized, in concentration of a few ppm. This clustering is too small to be detected by X-ray and FTIR spectra. There are also some mathematical models and methods used to simulate lithium diffusion and phase change in an iron phosphate-based LIBs in order to understand the cause for the low power capability of the material [79], such as first principle calculations [86, 87], shrinking-core model simulations [37, 79]. Some simulation results suggested $LiFePO_4$ is a semiconductor with a $\sim$0.3 eV band gap [88] and its conduction is one dimensional unlike $LiCoO_2$ and $LiMnO_2$ exhibiting 2D and 3D Li diffusion, respectively. First principles calculations also suggest that $LiFePO_4$ is limited by electron conduction and not Li^+ diffusion and that the activation barrier for Li hopping in $LiFePO_4$ (270 meV) is larger than that in $FePO_4$ (200 meV), which suggests that the $LiFePO_4$ cathode should be expected to have an asymmetric behavior between charge and discharge [87]. More recently, Shin-Ichi Nishimura group declared that lithium distribution along the [010] direction was clearly visualized by combing high-temperature powder neutron diffraction and the maximum entropy method [89]. This provides the long-awaited experimental evidence for such strong dimensional restriction of lithium motion in Li_xFePO_4, and it is considered as the first visual demonstration of the ion diffusion path in a battery electrode.

Challenging problems with $LiFePO_4$ for LIBS

Although great progresses have been achieved in improving the electrochemical performance of $LiFePO_4$ cathode material by carbon coating, minimization of particle size, and supervalent-cation doping, there are still some challenging problems that need to be solved before attempting to commercialize $LiFePO_4$ for the next generation of LIBs. Consequently, before the integration of advanced LIBs in HEVs, EVs or microbattery-powered systems is possible, the main challenging problems are to enhance the electronic conductivity, increase the Li^+ diffusion coefficient, attain high-rate capability at high-charge current density, achieve long cycling life, reduce fabrication cost, and solve safety issues, which embody the following aspects:

1. The current high costs and complexity of fabrication procedures motivate further development of cheaper and simpler methods to fabricate $LiFePO_4$ cathodes [38]. These will likely result from the combination of various optimization approaches;
2. At present, the low-temperature operability of $LiFePO_4$ has still not improved significantly [14]. The discharge capacity of Sanyo 18650 cells ($LiFePO_4$) is 888 mA h at 25 °C; however, it is only 375 mA h at 0°C. Fortunately, some progress has been made recently [14], the result demonstrates that electronic conductivity, low-temperature character, and the tap density of pre-prepared $LiFePO_4$–PAS composite were all improved. Yet, advanced LIBs will still have to be robust and operable at high temperature and under abusive conditions.
3. To understand the kinetic behavior of $LiFePO_4$ synthesis is certainly fundamental to optimize the synthesis conditions [51, 90]. Although optimization approaches have been proposed, the exact mechanism for the increased electronic conductivity, however, is still a subject of research [73, 91].
4. Electrochemical lithium intercalation/extraction properties of $LiFePO_4$, such as lithium-ion diffusion in $LiFePO_4$ and charge-transfer reaction at the electrode/electrolyte interface, have not been clearly understood, although they should play important roles in the charge-discharge performance [11, 42, 82, 84, 89].
5. Numerous questions remain to be answered concerning the fundamental origin of the kinetic limitations (ionic or electronic) in $LiFePO_4$ [71]. Such an effort would be useful in order to both identify the controlling mechanisms and suggest design changes that would improve the performance of $LiFePO_4$ [79].
6. It must be noted that fairly wide ranges of thermal conditions ranging from 550 to 800 °C with holding times ranging from 0.5 to 24 h, have been adopted to produce highly crystalline $LiFePO_4$. However, there are no reasonable explanation for these differences in synthesis conditions presently [90].
7. So far there has not been any systematic report or investigation of the underlying cause of the improvement of the electrochemical properties of $LiFePO_4$ (why those methods can be used to improve the performance of $LiFeO_4$) from the point of view of kinetics [52, 69]. To understand the fast electrochemical response from the poorly electronic conducting two-phase $LiFePO_4/FePO_4$ system is an intriguing fundamental problem [77, 84].

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