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Mini Review

Improving Methods for better Performance of Commercial $LiFePO_4$/C Batteries

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Olivine-type lithium iron phosphate ($LiFePO_4$) electrodes had the advantages of low cost, low toxicity, and high theoretical capacity, and have attracted the attention of those engaged in mass-production of commercial lithium ion batteries (LIBs). $LiFePO_4$/C secondary batteries were widely used in mobile devices, electric vehicles (EV) and energy storage power stations, and exhibited high energy density, stable cycle performance and low self-discharge rate at room temperature. However, $LiFePO_4$/C batteries suffered from rapid capacity deterioration at extreme low/high temperatures, which significantly limited their further commercial application. Therefore, it was of great significance to systematically summarize the accelerated fading mechanism of $LiFePO_4$/C batteries under extreme temperatures and the progress of the modification strategies. In this review, the degradation mechanism of $LiFePO_4$/C batteries at extreme low and high temperatures were discussed. Corresponding strategies in improving the electrochemical properties of $LiFePO_4$/C battery under these extreme conditions, including electrolyte optimization and cathode modification, were then grouped. Finally, several viewpoints were summarized based on the current progress, aiming to provide possible methods and research suggestions to enhance the practicality of commercial $LiFePO_4$/C batteries at extreme temperature conditions in the future.

Keywords: Lithium ion batteries, $LiFePO_4$, temperature, fading mechanism, improving strategies

1. INTRODUCTION

Since the beginning of the 21st century, the energy and environment crisis has become increasingly serious. And the development of new energy storage equipment was considered as one of the main solutions. Lithium-ion batteries (LIBs), as one of the most stable energy storage equipment, played a key role in effectively storing energy and providing power for various devices such as electric vehicles [1~5]. Thanks to the notable advantages [6-10], including high theoretical capacity (170 mAh/g), stable cyclability and environmental friendliness, $LiFePO_4/C$ secondary batteries received considerable attention and were widely used in mobile equipment, electric vehicles (EV) and energy storage power stations. However, the inherent defects, including the low electronic conductivity (10^{-8} to 10^{-10} s/cm) [11,12] and slow Li-ion diffusion rate (10^{-14} to 10^{-16} cm^2/s) [13], narrowed the acceptable work temperature of $LiFePO_4$ batteries. Once working outside of the temperature zone, the batteries would fade rapidly, and even posed safety risks, such as fire and explosion, which limited the commercialization of batteries.

In this review, the impact of temperature on the degradation of $LiFePO_4/C$ secondary batteries, together with various strategies to overcome this fatal shortcoming were summarized. Generally, there were two main aspects of the temperature impact: low temperature electrochemical performance (LTEP) and high temperature electrochemical performance (HTEP) [14-17]. As shown in Fig. 1, low temperature would decrease the Li^+ diffusion and electronic conductivity, and increase the loss of active lithium. The elevated temperature, by contrast, would promote the decomposition of $LiFePO_4$ and electrolyte, accelerate of the consumption of active lithium, and increase the interfacial resistance. These undesirable effects accelerated the fading of LIBs and even caused more and more safety issues. Therefore, reasonable strategies to reduce the temperature impact were essential for the commercialization of $LiFePO_4/C$ batteries. Currently, the main strategies to overcome the impact of temperature on the electrochemical performance of $LiFePO_4/C$ batteries were focused on improving the Li^+ diffusion rate and electronic conductivity in the $LiFePO_4$ electrode at low temperature, as well as increasing the stability of electrolyte and cathode at high temperature.

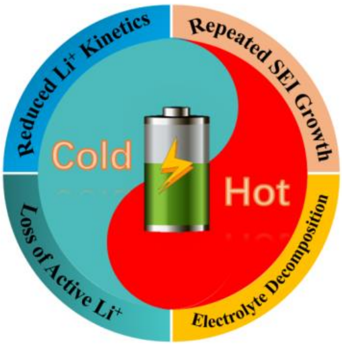

Figure 1. The deterioration factors of $LiFePO_4/C$ batteries at high/low temperatures.

2. FADING MECHANISM AND THE IMPROVEMENT STRATEGIES AT LOW TEMPERATURE

2.1 Fading mechanism

Similar to other phosphate materials, $LiFePO_4$ had intrinsic low electronic conductivity and ion diffusion rate. In high latitudes and high-altitude areas, such as Antarctica, low temperature further reduced the charge transfer kinetics. In particular, the performance of mobile equipment, electric vehicles (EV) and energy storage power stations was restricted. In 2008, Liao [18] firstly described the severe fading of $LiFePO_4$/C batteries at low temperature, and attributed the accelerated aging process to the decreased Li^+ diffusion in the electrodes by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) analysis.

Generally, the intercalation of Li^+ in graphite anodes competed with the lithium plating on the surface of the anodes. Low temperature decreased the diffusion of Li^+ in the graphite particles and induced the over-saturation of lithium, which could increase the growth of lithium plating. Petzl [19] concluded that the lithium plating on the anode surface catalyzed the growth of SEI and caused the increase of the interfacial resistance, which was the potential aging reason of $LiFePO_4$/C batteries. Incremental capacity analysis (ICA) was performed by Ouyang [20] to confirm that the loss of active lithium rather than the decay of electrodes accelerated the aging. The observed needle-shaped lithium on the anode surface and the introduced mathematical model verified this process. Moreover, they found the charging rate and cut-off voltage range played an important role in the loss of active lithium and the resulted degradation. Those findings led to the follow-up work of Zheng [21], who studied the effect of the charging rate (1/10 C, 1/3 C, 1/2 C, and 1C) on the fading of $LiFePO_4$/C batteries at low temperature by nondestructive tests and postmortem analysis. Their work confirmed that the lithium deposition increased the ohmic resistance by catalyzing the growth of solid electrolyte interface (SEI) film. And the increased charging rate and cycle numbers accelerated the capacity fading of the LIBs. Besides, lithium plating induced electrodes detachment from the current collector further enhanced the degradation of $LiFePO_4$/C batteries at low temperature [22]. Therefore, an important mechanism for the failure of $LiFePO_4$/C batteries at low temperature was the increased ohmic resistance, as a result of the growth of SEI.

Under working, the crystal phase dynamically changed during the lithium extraction/insertion process. Some parameters, such as the high-rate current and low temperature, changed the Li^+ reaction from thermodynamic control to kinetic control for forming a non-equilibrium Li_xFePO_4 solid solution variation [23]. Mai [24] studied the non-equilibrium phase transition process of $LiFePO_4$ cathode by in-situ X-ray diffraction (XRD) at various temperatures. Specifically, the path at room temperature showed the traditional phase boundary model, which required less energy during the equilibrium thermodynamics process about the phase change between $FePO_4$ and $LiFePO_4$. By contrast, the path at low temperature required higher energy, which was verified via a supersaturation model of continuous solid solution. The improved energy pathway between $LiFePO_4$/$FePO_4$ phases change indicated ion diffusion coefficient was reduced, and the reaction was limited with the decreased temperature. Therefore, the reduced reaction kinetics of Li^+ was other reason for the failure of $LiFePO_4$/C batteries at low-temperature.

Commercially, carbon coating method was generally used to increase the charge transfer kinetics and achieve the improvement of the electrochemical performance of $LiFePO_4$ cathode. Nevertheless, Liu [25] found the increasing carbon content cannot continuously improve the LTEP of the carbon-coated $LiFePO_4$ ($LiFePO_4$@C) based LIBs batteries. And the subsequent conductivity measurement proved that the electronic conductivity determined the LTEP of naked $LiFePO_4$

secondary batteries, while the LTEP of the carbon-coated $LiFePO_4$@C secondary batteries was limited by the ionic diffusion rate in the electrolyte.

To summarize, previous studies have demonstrated that the degradation of $LiFePO_4$/C secondary batteries at low temperature was resulted from the following factors: (i) the increased ohmic resistance due to the growth of SEI film; (ii) reduced Li^+ reaction kinetics and electronic conductivity and (iii) the limited ionic diffusion rate in the electrolyte. Based on the above deterioration mechanism, the modification strategies for improving the LTEP of $LiFePO_4$ batteries were proposed correspondingly, including warming up the batteries, electrolyte optimization and electrode modification etc., which were systematically discussed in this review.

2.2 Strategy I: Rapidly and safely warming up the LIBs

Since the low temperature impact for $LiFePO_4$/C batteries was mainly from the cold working environment, the simplest strategy to overcome the brought shortcomings was to warm up the batteries. Self-heating method could eliminate the loss of heat from the equipment and avoid the thermal runaway to a large extent. Therefore, a simple internal heating method was of great significance to improve the LTEP of $LiFePO_4$/C batteries. Pulse charging method could effectively prevent the lithium saturation to generate more heat, which was resulted from the improved reaction kinetics of the increased active lithium. Notten [26] proposed that pulse charging protocols with microsecond pulse-time generated more heat in the $LiFePO_4$/C batteries by a mathematical model. Chen [23] explained that pulse current could prevent the saturation of interface lithium to generate more reaction-induced heat by introducing a mathematical model. Based on the above analysis, authors introduced an additional excitation stage of pulse current to pre-heat the $LiFePO_4$/C secondary batteries before charging with the conventional constant current-constant voltage (CC-CV) mode. It was found that the surface temperature of $LiFePO_4$/C secondary batteries rapidly increased from -10 ℃ to 3 ℃ at the pre-heating stage. Comparing to the traditional charging mode, the total charging time with pre-heating was reduced by 23.4%, but the capacity increased by 7.1% at low temperature. Therefore, the pre-heating stage from the pre-excitation of pulse current was beneficial to charge $LiFePO_4$/C secondary batteries safely and quickly at low temperature.

To improve the practicability of the pulse current heating method, Gu [27] studied the influence of the current parameters on the heating effect. It was found that higher current intensity, lower frequency and wider voltage range could promote the heat accumulation in $LiFePO_4$/C batteries without any damage to the state of health (SOH).

2.3 Strategy II: Electrolyte optimization

The electrolyte not only determined the ionic mobility, but also participated in the growth of solid electrolyte interfaces (SEI) on the electrode [28]. Therefore, it should be technically feasible to reduce the interfacial resistance by modifying the electrolyte. $LiPF_6$, as the most widely used electrolytic salt in commercial LIBs, would decompose and generate non-conductive LiF in the SEI, thereby increasing the interface resistance to reduce the LTEP of the LIBs. Developing new electrolytic salts to replace $LiPF_6$ was adopted by many researchers to improve the LTEP of $LiFePO_4$ batteries. For example, Luo [29] replaced $LiPF_6$ with the mixture of lithium difluoro (oxalate) lithium borate (LiODFB) and sulfolane (SL) and improved the capacity retention efficiency of $LiFePO_4/C$ batteries from 9.8% to 32.0% at the initial cycle under -40 ℃. Compared with commercialized $LiPF_6$-EC/DMC electrolyte, LiODFB-SL/DMS formed SEI film with lower resistance due to the formed sulfide compounds, thereby increasing the electronic conductivity at low temperature. $LiCO_3$ was well known SEI film forming additive in LIBs, and Wu [30] introduced it to improve the specific at -20 ℃ by decreasing the polarization and activation energy during the charge transfer process, as shown in Fig. 2. This study showed that modifying the electrolyte composition was a potential solution to improve the LTEP of $LiFePO_4/C$ batteries.

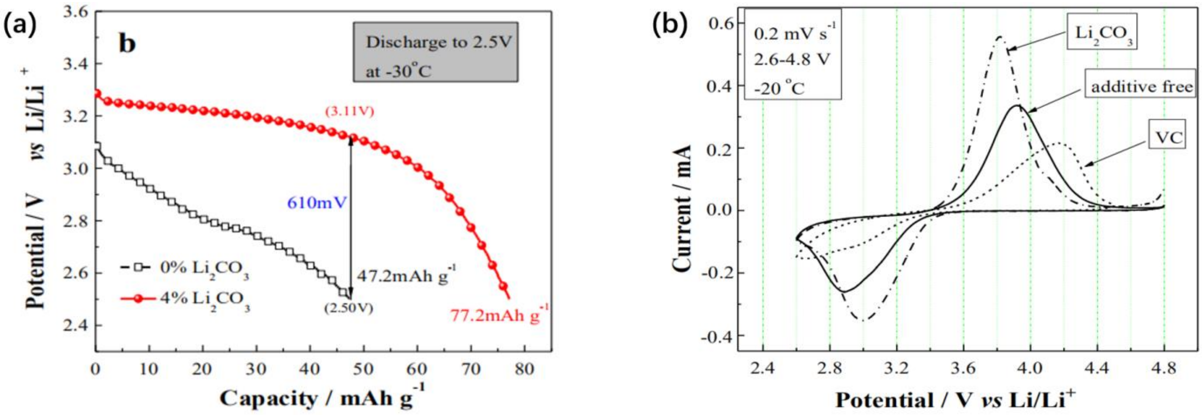

Figure 2. (a) Discharge profiles of $LiFePO_4/C$ cell in the electrolytes with 0% and 4% Li_2CO_3 at -30 ℃. (b) CV curves of $LiFePO_4$ electrode in the electrolyte without and with different additives at a sweep rate of 0.2 mV/s at -20 ℃. Reproduced with permission from Ref. [30]. Copyright 2013, ESG.

Changing the composition of the electrolyte required the systematical adjustment of the solvent and electrolytic salt. Alternatively, Yin [31] simply added fluoroethylene carbonate (FEC) to the electrolyte. It was found that 2 wt% FEC could effectively enhance the discharge capacity and rate property of $LiFePO_4/C$ batteries under -20 °C. Subsequently, Wu [32] revealed that FEC participated in the formation of SEI film, in which the content of $Li_xPO_yF_z$, LiF, and carbonate species was significantly reduced. This indicated that the decomposition of $LiPF_6$ and electrolyte was weakened and the interface resistance caused by LiF was reduced, by which the diffusion of Li^+ was enhanced. In addition to FEC, other electrolyte additives were developed, such as Butyl Sultone (BS) [33], by participating in the formation of a lower-resistant SEI film, showed similar effects to FEC in improving the LTEP of $LiFePO_4/C$ batteries.

Unfortunately, there were only very few systematic and comprehensive studies on improving the application of $LiFePO_4/C$ batteries based on electrolyte optimization, especially at low temperature. Therefore, it was necessary to conduct more experimental and theoretical studies on electrolytes at low temperature to improve the LTEP of $LiFePO_4/C$ batteries by proposing more optimization methods.

2.4 Strategy III: Electrode Modification

The intrinsic low electronic conductivity of $LiFePO_4$ cathode was an adversity, and low temperature exacerbated this shortcoming [34]. Surface coating was an effective and controllable method to build an artificial conductive layer and enhance the Li^+ diffusion in the bulk of electrode, which suggested researchers to improve the LTEP of $LiFePO_4$ cathode by surface modification with carbon or other conductive additives [35]. For example, Guo [36] and Wu [37] coated $LiFePO_4$ with carbon nanotubes and carbon nanofibers to improve the LTEP of $LiFePO_4$ cathode. These methods all improved the LTEP of the $LiFePO_4/C$ batteries by improving the electron transfer rate in the electrode.

Coating carbon layers and reducing the nanoparticles size have been wildly applied in industry to enhance the electronic conductivity and decrease the particle size of $LiFePO_4$. However, low-temperature property of carbon-coated $LiFePO_4$ ($LiFePO_4$@C) cathode was still needed to be improved [38]. Surface modification with conductive metal oxides, such as V_2O_3 as the third modification phase, could increase the graphitization degree of the carbon layer on the $LiFePO_4$@C cathode surface [39]. The Li^+ diffusion coefficient proved that the carbon-V_2O_3 layer significantly facilitated the Li^+ transport in the $LiFePO_4$@C, and thus improved the specific capacity of the cells from 60.0 to 135.0 mAh/g at the initial cycle. Subsequently, Su [40] found that the surface coating of CeO_2 on the $LiFePO_4/C$ surface could improve the capacity retention of the cells from 58.0％ to 64.8 ％ at 2 C under -20 ℃ by enhancing the Li^+ insertion/extraction kinetics in the cathode. Chueh [41] attributed this improvement to the internal adsorption of ions on the CeO_2 surface, which caused cation vacancy at the interface of $LiFePO_4$ and resulted in the enhanced Li^+ diffusion kinetics.

Surface modification was proved to be an efficient way to bridge the active particles with the conductive additives and construct a conducting network. Ti_3SiC_2, as a typical $M_{n+1}AX_n$ material with a sheet structure, was adopted to establish a “plane-to-point” conducting mode to provide paths for electron transfer instead of “point-to-point” mode between spherical $LiFePO_4$@C particles. The content of the added Ti_3SiC_2 determined the improvement, and TSC-4 (4 wt%) showed the most prominent effect on the improvement [42, 43]. Compared with the inorganic materials, organic polymers owned some special advantages as modified materials, including easy fabrication of three-dimensional conductive frameworks and porous structures, which were beneficial for the extraction/insertion of Li^+. Zhu [44] found that the modification of conductive PPy could improve the low-temperature electrochemical performance of $LiFePO_4$ cathode by shortening the diffusion path of Li^+ extraction/insertion, as shown in Fig. 3.

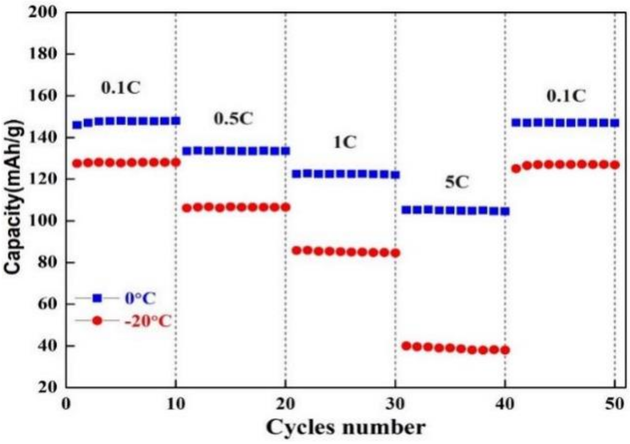

Figure 3. The comparison of cycling performance of $LiFePO_4$/PPy cathode at 0°C and -20 °C at various rates with PPy content of 2.95%. Reproduced with permission from Ref. [43]. Copyright 2019, ESG.

However, these common coating approaches could not enhance the electronic conductivity and lithium diffusion coefficient within the crystal. In addition, these works would cause additional drawbacks, including the loss of energy density due to the electrochemically inactive coating additives. Chung [45] firstly constructed super-valent ions doped solid-solution to improve the electronic conductivity within the $LiFePO_4$ lattice. The obtained composite showed near-theoretical energy density, and retained high capacity at a current density of 6,000 mA/g. The authors attributed the improvement of electronic conductivity to the occupied site of Li (M1), which leaded to the co-existence of Fe^{2+} and Fe^{3+} in single phase. Some cations, including the rare earths [46] and metallic elements [47], were then suggested to dope in the $LiFePO_4$ cathode and occupy the Li (M1) site to enhance the electronic conductivity. In addition to the replacing of Li site, Roberts [48] reduced the crystal size of $LiFePO_4$ by replacing Fe with Mg and improved the capacity of the cathode. The enhanced electrochemical performance was thanks to the shortened electronic transfer paths within the active material particles, and the modified sample morphology would reduce the agglomerates of particles. Subsequently, some common metal ions, such as Ni^{2+} [49] and Mn^{2+} [50], were suggested as doping ions to occupy the Fe site. Porous structure was favorable to improve the specific capacity of $LiFePO_4$/C cells at various rates through improving Li^+ diffusion. For example, Jiang [51] fabricated carbon aerogel (CA) templated and the lanthanum (La^{3+}) and magnesium (Mg^{2+}) co-doped $Li_{0.99}La_{0.01}Fe_{0.9}Mg_{0.1}PO_4$/CA composite to realize the application of $LiFePO_4$/C cells under low temperature. The cation defects caused from cation doping facilitated the diffusion of Li^+ and the electronic conductivity within the crystal. Moreover, the diffusion of Li^+, depending on both the contact area and diffusion paths, was enhanced by the porous CA “bridge”.

Not only cations, but also anions-doping was also studied in improving the electrochemical performance of $LiFePO_4$ cathode. For example, Pan [52] doped F^- into the $LiFePO_4$ nanoparticles by a hydrothermal method, which improved the electronic conductivity and stabilized the crystal structure of $LiFePO_4$ phase. Detailly, F-doping improved the length of the Li-O bond and weakened the bond energy, which improved Li diffusion kinetics between the $LiFePO_4$ phase and the $FePO_4$ phase. This inspired Lv [53] to mix V^{3+} and F^- to co-dope $LiFePO_4$@C cathode, and they found that the number of empty spaces increased with the doping, which would enhance the charge transfer kinetics and the LTEP of $LiFePO_4$/C composite. As a result, the specific capacity and of the rate performance were improved. Subsequently, co-doped materials such as $LiFe_{0.92}Mg_{0.08}$ $(PO_4)_{0.98}F_{0.03}$ [54] was prepared. Compared with the bare $LiFePO_4$, its specific capacity improved from 39.0 to 73.0 mAh/g, which was resulted from the improved lithium diffusion and electronic conductivity. Besides, P doped $LiFePO_4$/C cathode showed similar improvement performance with F, as the results of charge transfer kinetics and the enhanced stability of $LiFePO_4$@C electrode [55].

Generally, surface coating methods provided higher specific capacity than pristine $LiFePO_4$ cathode in low temperature due to the reduced charge transfer resistance. And optimized element doping strategies could effectively improve the lithium diffusion inside the $LiFePO_4$ crystal to alleviate the serious capacity degradation of $LiFePO_4$ cathode at low temperature. Therefore, the combination of element doping and surface treatment might be a reasonable choice, and further research was urgently needed.

3. FADING MECHANISM AND THE IMPROVEMENT STRATEGIES AT HIGH TEMPERATURE

3.1 Fading mechanism at high temperature

$LiFePO_4$/C batteries often exposed to working temperature as up to 60 °C to meet the needs of various applications. In addition, high-rate charge/discharge process generated excessive heat, which made it more important to systematically summarize the research progress of failure mechanism of the cells at high temperature. Belharouak [56] studied the HTEP of $LiFePO_4$/C secondary batteries and found that high operating temperature accelerated the capacity fading. Energy dispersive X-ray analysis (EDAX) showed that during the aging process, the interface resistance increased with the deposition of Fe on the anode surface. Therefore, they attributed the high temperature-dependent of the cells degradation to the impedance rise of the electrodes resulted from the catalyzed growth of SEI by the deposited Fe. Through the analysis of XRD, SEM, TEM and XPS test results, Yin [57] proposed that in addition to the increased interface resistance caused by the growth of SEI film, the structural degradation of the cathode material caused by the dissolution of Fe^{2+} was another potential reason for the failure of $LiFePO_4$/C batteries at high temperature.

However, Liu [58] put forward that the capacity decay of the $LiFePO_4$ cathode caused by the dissolution of Fe^{2+} was not enough to decrease the capacity of the commercial $LiFePO_4$/C batteries. Rather, they proposed that the loss of active lithium caused by the repeated growth of SEI film at high temperature was the main reason. To verify this view, Chen [59] added functional additives (LiBOB/VC) to the electrolyte of $LiFePO_4$/C batteries to suppress the dissolution of Fe^{2+}, and the results showed that the capacity fading of the batteries was still high-temperature dependent. They concluded that the improved temperature accelerated the active lithium consumption during the reformation/repairing of SEI film, which was considered as another reason for the fading of $LiFePO_4$/C batteries at high temperature. The temperature-dependent lithiated Li_xFePO_4 phase of the cathode confirmed the view.

$LiPF_6$ was the most common electrolytic salt. Through X-ray photoelectron spectroscopy (XPS) spectra, Lindbergh [60] found that high temperature would increase the deposition of oxidized $LiPF_6$ decomposition at the electrodes surface. Besides, $LiPF_6$ was easily to be hydrolyzed to generate hydrofluoric acid (HF) ($LiPF_6 + H_2O \rightarrow 2HF + LiF + POF_3$), which would corrode the $LiFePO_4$ cathode [61]. And high temperature would accelerate this process. As a result, the electrode resistance increased as the precipitated Fe increased, and the calculated Li^+ diffusion coefficient decreased severely. This indicated that the Fe deposition accelerated the fading of $LiFePO_4$/C batteries by catalyzing the growth of SEI, rather than changing the crystal structure of the cathode material. This coincided with the view of Belharouak et al.

Therefore, it was concluded that the accelerated fading of $LiFePO_4$/C batteries at high temperatures was mainly attribute to: (I) the increased interfacial resistance from the growth of SEI; (II) the loss of active lithium; (III) the decomposition of electrolyte. The above degradation mechanism inspired researchers to propose different strategies to enhance the cyclability and thermal stability of $LiFePO_4$ batteries at high temperature. These strategies mainly included electrolyte optimization and electrode modification, which would be discussed detailly in the following.

3.2 Strategy I: Modifying the electrolyte

Beside the attacks on the $LiFePO_4$ spinel surface, the resultant decomposition of $LiPF_6$ could enhance the interfacial resistance on the electrode surface. Therefore, great efforts have been devoted to optimize the electrolyte of $LiFePO_4$/C batteries, including developing alternatives of $LiPF_6$ to eliminate HF, as well as developing functional additives to stabilize the electrolyte and modify the SEI layer. Belharouak [57] proposed that the usage of an electrolyte salt without F element could inhibit the leaching of Fe^{2+} from the surface of $LiFePO_4$. In their study, they replaced $LiPF_6$ with lithium bisoxalatoborate (LIBOB) salt and found that both the deposition of Fe particles on the graphite anode and the deterioration of the $LiFePO_4$/C batteries at high temperature were significantly decreased. As a result, the capacity retention of the batteries improved from 36.2% to 79.8%. However, the low solubility of LIBOB in linear alkyl carbonate and the resulted high viscosity increased the internal resistance of LIBs, which limited the LTEP of $LiFePO_4$ secondary batteries. Although $LiBF_4$ could not improve the HTEP of the LIBs, its low viscosity was able to reduce the charge transfer resistance and promote the reaction at the electrode interface, thus improving the LTEP of $LiFePO_4$/C batteries. To broaden the working range of LIBOB electrolytic salt, Zhang [62] mixed LIBOB with $LiBF_4$ to form $LiBF_4$-LiBOB mixed salt and added in the electrolyte of $LiFePO_4$/C batteries.

Their approach enabled $LiFePO_4$/C batteries to operate stably in a wider temperature range (-40~80 ℃) with excellent power density. Because of the highly thermal stability, lithium-bis(trifluoromethanesulfonyl) imide [LiTFSI, LiN $(CF_3SO_2)_2$] was expected to replace $LiPF_6$ salt to improve the HTEP of LIBs [63]. However, when LiTFSI was used in the electrolyte, the aluminum current collector was corroded at about 3.7 V [64]. It was found that the formed Al-TFSI (Al-(trifluoromethanesulfonyl) imide) compounds on the surface of aluminum foil was the main reason to cause the corrosion. Therefore, Zhang [65] introduced additional LiBOB to form a stable film on the Al foil to prevent the corrosion. Moreover, they found that the cycle stability of $LiFePO_4/C$ batteries was improved by introducing the optimal mixture of LiBOB (50 wt%) and LiTFSI (50 wt%) in to the electrolyte.

The introduction of functional additives would greatly simplify the process of improving the electrolyte performance. Anion receptors, such as tris (pentafluorophenyl) borane (TPFPB), were believed favorable to mop up free F^- and were proposed as electrolyte additives for LIBs to increase the cyclability at high temperature [66, 67]. Chang [68, 69] introduced this mechanism and found that the additive of TPFPB could decrease the LiF content in the SEI film and the formation of HF in the electrolyte. As a result, the electrolyte with TPFPB improved the capacity retention from 23.1% to 46.2% after 100 cycles at 60 °C. Besides, Her [70] found that methyl-substituted borate anion acceptor compounds improved the capacity retention of $LiFePO_4/C$ batteries from 7% to 53% after 100 cycles at 60 °C. This was because the anion binding site of the borate anion acceptor contained an electron-deficient B atom coordinated with an electron-withdrawing group. XPS proved that methyl-substituted borate anion acceptor reduced the formation of inorganic species on the electrode surface, such as LiF, Li_xPF_y and $Li_xPO_yF_z$.

As summarized, the decomposition of the electrolyte was one of the main factors that cause serious decay of $LiFePO_4$ cathode at high temperature. Therefore, developments of new electrolytic salt and functional additives were effective means to move the undesirable HF and to alleviate the electrolyte decomposition at elevated temperatures.

3.3 Strategy II: Electrode modification

In addition to the functional electrolyte additives, surface modification of the electrodes was also proved as an excellent method to eliminate the dissolution of Fe^{2+} from $LiFePO_4$ and reduce the resistance from the SEI growth. For example, metal layers (such as copper and gold) were deposited on carbon anodes worked as ion-sieving layers to collect Fe^{2+} during cycling. And the collected metallic Fe particles could no longer catalyze the formation of SEI, thereby reducing impedance and reducing capacity degradation [71]. Amorphous silicon (α-Si) was a short-range ordered structure, and contained some dangling bonds, which shortened the distance of charge transfer. Therefore, Huang et al. [72] modified carbon-coated $LiFePO_4$ ($LiFePO_4$@C) particles by depositing α-Si film on its surface. It was found that, in addition to reducing the direct contact between the cathode and the electrolyte, the silicon dangling bonds in α-Si film would consume the amount of free H^+ to reduce the generation of HF in the electrolyte. As a result, the specific capacity of $LiFePO_4$@C batteries was improved from 140 to 155 mAh/g at 0.2C after 25 cycles. And it was verified that the improvement of $LiFePO_4$@C/α-Si was attributed to the decreased electrode polarization, improved lithium ion diffusivity in the cathode, as well as the enhancement of electrode reaction reversibility.

Subsequently, Li [73] coated $LiFePO_4$@C with SiO_2 layers by a sol-gel method. And they found that the coating improved the cycle stability of the cells by enhancing the charge transfer kinetics. In addition to reducing the resistance and the direct contact of the $LiFePO_4$ particles with the electrolyte, they also believed that the SiO_2 coating played a regulatory role for Li^+ inserting the $LiFePO_4$ by increasing the additional order of the outer lattice in the particles. Compared with the pure element layers, the inorganic compound layers deposited by traditional plating method played the same role. Moreover, due to the advanced processing technology, this type of inorganic layer was beneficial to be applied to mass-scale preparation of the modified $LiFePO_4$. For example, Liang [74] used traditional atomic layer deposition method to coat TiN on the surface of $LiFePO_4$. The modified $LiFePO_4$ batteries showed a higher specific capacity (78.8 mAh/g) than that of the un-coated $LiFePO_4$, which was resulted from the enhanced electrode density, improved electronic conductivity and the protective nature of the ALD thin film coating. Li-rich oxides showed enhanced cyclability and coulombic efficiency for affording numerous available sites to insert Li^+, such as spinel $Li_4Ti_5O_{12}$ (LTO). Some efforts have been devoted to coat cathode materials with LTO to enhance the electrochemical performance. For example, Sun [75] reported that a 4 wt.% LTO-coated $LiMn_{1.4}Ni_{0.4}Cr_{0.2}O_4$ particle exhibited an improved electrochemical performance. Inspired by this idea, Jiang [76] coated $LiFePO_4$@C cathode with various amount of LTO, and found that 3 wt.% LTO-coated $LiFePO_4$@C composite improved the stable capacity from 67.0 to 97.0 mAh/g after 200 cycles under 55 ℃. The constructed dual-layers were comprised of an electron-conducting layer (carbon) and an ionic conducting layer (LTO), which was proved to be the reasons of the improved cycling stability at elevated temperatures.

A reasonable surface coating layer could suppress HF attack and avoid Fe dissolution. Further element doping strategies could enhance the electronic conductivity of the surface decorated electrode at elevated temperature. Therefore, the combination of element doping and surface decoration strategies should be a reasonable choice and urgently required for further investigation.

4. CONCLUSION

Due to the inherent defects, $LiFePO_4$ battery exhibited severe degradation under excessive high/low temperatures. Here, we investigated and summarized the major factors that are responsible for accelerating the low-temperature/high-temperature fading of $LiFePO_4$ batteries. At low temperature, the decreased charge transfer kinetics and increased interfacial resistance limited the performance of $LiFePO_4$ batteries. Therefore, the main strategies to improve low-temperature performance were focused on pre-heating the batteries safely and quickly and modifying the electrolyte and electrode materials to reduce lithium ion transfer resistance. The rapid decay at high temperature was mainly due to the dissolution of Fe^{2+} from the $LiFePO_4$ electrode, the loss of active lithium, and the decomposition of the electrolyte. Therefore, improving the stability of electrode and electrolyte was essential in improving the battery performance at elevated temperatures. The mechanisms and strategies summarized here were helpful to improve the practicality of $LiFePO_4$ batteries, especially to broaden its application in extreme environments, such as Antarctica and equatorial regions.

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