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Mini Review

Surface modification of $LiFePO_4$ by Coatings for Improving of Lithium-ion Battery Properties

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High-energy-density, high-safety, long-cycle-life and low-cost lithium-ion batteries are urgently needed for electric vehicle power batteries and energy storage battery markets. As a candidate cathode material, $LiFePO_4$ has attracted extensive attention because of its high theoretical capacity, high safety and low cost. Unfortunately, $LiFePO_4$ suffers from low tap density, poor intrinsic electronic and ionic conductivity, and a slow Li^+ diffusion coefficient. On the subject, the surface coating is considered an available method. A suitable surface coating can enhance the surface structure stability of the $LiFePO_4$ material, accelerate the electron and Li^+ migration, prevent the side reaction between $LiFePO_4$ electrode and electrolytes and protect $LiFePO_4$ from HF corrosion. Hence, the article discusses the research progress of several typical surface coating materials to improve the electrochemical performance of $LiFePO_4$ in recent years to supply a guide for optimizing the performance of other battery materials.

Keywords: Lithium-ion batteries; $LiFePO_4$; Surface coating; Electrochemical performance

1. INTRODUCTION

In today's energy structure, the energy used by human beings is mainly fossil energy with huge carbon emissions, such as oil, natural gas and coal. In recent years, greenhouse gases have brought disasters to the earth and human environment. “Carbon reduction” and “carbon neutrality” are gradually understood and accepted. Therefore, the development of new energy is of great significance. Only by adjusting the energy structure, reducing the proportion of fossil energy, and expanding the use scale of solar, wind, tidal and lithium-ion batteries, etc. can the long-term goal of carbon emission reduction and green mountains be better achieved. The $LiCoO_2$/graphite of lithium-ion batteries was introduced by SONY in 1991 [1]. When $LiCoO_2$ is used as a cathode material, the Li_xC_6 compound is formed through the graphitized carbon for the anode and insertion of lithium ions, which avoids the internal short circuit caused by dendrites when lithium metal is used as the anode. Lithium-ion batteries have been widely applied to digital products, electric vehicles and energy storage devices due to their high energy density, remarkable cycle life and environmental friendliness. Lithium-ion batteries are mainly composed of cathode materials, anode materials, separators, electrolytes and shells. Cathode materials are generally intercalated lithium transition metal oxides, which directly affect the performance of lithium-ion batteries [2-6].

Phosphates ($LiMPO_4$, M=Fe, Mn, Co) with olivine structures were discovered by Padhi and Goodenough in 1997 [7-9]. Compared with traditional cathode materials for lithium-ion batteries, $LiFePO_4$ delivers superior cycle life, high safety and wonderful overcharging tolerance. As a result, it has become the current mainstream cathode material. However, the low tap density, slow Li^+ diffusion coefficient, poor intrinsic electronic and poor ionic conductivity have restricted its widespread applications [10-13]. To resolve these problems, modifications including surface coating, metal doping, morphology control and particle size reduction have been exploited [14-18]. Metal doping can improve the electrical conductivity of $LiFePO_4$. However, thus far, the actual role of metal doping has been complex and controversial. Additionally, the particle size reduction can shorten the Li^+ diffusion path. Unfortunately, the higher surface area demands more binders during electrode fabrication, which increases cell polarization. Moreover, decreasing the particle size will decrease the tap density [19]. Among these modifications, surface coating has been considered an extremely effective strategy to enhance the electronic conductivity and improve the electrochemical properties of the $LiFePO_4$ cathode. The ideal surface coating for $LiFePO_4$ should be ionic and electronic conductors while protecting the electrode from HF corrosion. Numerous reports have presented surface coatings ranging from carbon to solid electrolyte coatings [20-25]. Nevertheless, the surface coating must be further understood. This work overviews the latest progress in the development of major types of surface coating materials for $LiFePO_4$ while providing prospects for electrode materials in next-generation batteries.

2. ROLE OF SURFACE COATING

The biggest disadvantage of $LiFePO_4$ with PO_4^{3-} polyanions is the low electrical conductivity, which causes significant polarization during charging and discharging. If the conductive agent cannot be uniformly dispersed, the capacity of $LiFePO_4$ will be significantly reduced. Since the potential of the anode for lithium-ion batteries is close to that of lithium, it is relatively active and unstable in aqueous systems. Therefore, a nonaqueous liquid $LiPF_6$-based electrolyte was used. However, $LiPF_6$ may decompose to PF_5, which reacts with trace amounts of water impurities in lithium-ion batteries to form HF [26-27]. $LiFePO_4$ particles are in direct contact with the electrolyte and may be attacked by HF [28-29]. Surface coating is a potential method to enhance the performance of $LiFePO_4$.

The electrochemical performance of the original $LiFePO_4$ largely depends on factors such as the quality, amount of coating and nature of the coating material. There are multifarious coating strategies, including the solid-state method, sol-gel technique, and magnetron sputtering. [30-34]. According to the various synthesis processes, the synthesized materials exhibit different characteristics. The functionalities of surface coatings are summarized as follows: (1) Improving the surface stability for $LiFePO_4$ material. Particle fatigue during continuous cycling is effectively prevented, and the structural stability is maintained, which greatly improves the cycling property of $LiFePO_4$. (2) Enhancing the electronic contact between particles and ionic conductivity. Surface coating can facilitate the rapid transfer of Li^+ and electrons, which reduces charge transfer resistance and increases the Li^+ diffusion coefficient. (3) Inhibiting the side reactions between the $LiFePO_4$ electrode and electrolytes, particularly at elevated temperatures. (4) Protecting the $LiFePO_4$ electrode from HF corrosion. Surface coating prevents $LiFePO_4$ particles from directly contacting the electrolyte and diminish the dissolution of iron.

3. TYPES OF SURFACE COATING MATERIALS

The electrode reaction occurs at the electrode/electrolyte interface, and the electrochemical properties of the $LiFePO_4$ material can be modified by surface coating. Common surface coating materials include carbon, metals, metal oxides, solid electrolytes, ion conductive materials, cathodes and anode materials. The effects of the primary coating materials on the properties of $LiFePO_4$ are elaborated below.

3.1. Carbon

Carbon coating is one of the most commonly adopted methods to improve the specific capacity and rate performance because of its high conductivity, low cost and easy implementation. In addition to pure carbon coatings, modified carbon coating layers such as doping have attracted extensive attention [14]. Carbon materials comprising inorganic carbon materials (e.g., graphene, carbon nanotubes (CNTs)) and organic carbon materials (e.g., polyvinyl alcohol (PVA), polyaniline (PAni), and glucose) can prevent the oxidation of Fe^{2+}, inhibit the contact of internal particles, and suppress the growth of abnormal grains. The advanced electronic conductivity of the material will also be achieved. In addition, the growth of $LiFePO_4$ grains can be restrained as a nucleating agent, which improves the ionic conductivity with a shortened Li^+ diffusion path.

3.1.1. Inorganic carbon materials

Graphene is a unique inorganic carbon material in which sp^2 hybrid connected carbon atoms are tightly packed into a single two-dimensional honeycomb lattice structure. The electrons can smoothly conduct between layers, so graphene delivers excellent electrical conductivity and the lowest electrical resistivity of known materials. Moreover, graphene has a high specific surface area and superior flexibility. In 2004, Novoselov et al. [35] prepared monolayer graphene by mechanical stripping for the first time, and its special electrical and mechanical properties were discovered. Over the years, it has been employed as an additional material to improve the electrochemical performance of cathode materials and exhibits good application potential in lithium-ion batteries. In particular, the electronic conductivity and ionic conductivity of the $LiFePO_4$ cathode have been enhanced via graphene surface decoration.

The $LiFePO_4$/graphene nanocomposite was fabricated via a hydrothermal method with stirring and dropping by Zhang's group [36]. A higher electrical conductivity (1.75×10^{-5} S cm^{-1}) for $LiFePO_4$ with graphene coating was obtained, which indicates a lower charge transfer resistance. The calculated Li^+ diffusion coefficient (D_{Li}) was 2.15×10^{-13} cm^2 s^{-1} at -30 °C. The nanocomposite delivered a higher capacity of 93.6 mA h g^{-1} (0.5 C) at -30 °C and better rate performance at low temperature. As a result, graphene is considered an anticipant carrier to facilitate electron transfer and Li^+ diffusion. Unfortunately, its electric conductivity is easily reduced by bringing oxygen functional groups into the defect site. Doping is an available method to adjust the electrical properties of graphene. Luo et al. [37] prepared $LiFePO_4$ modified with N-doped graphene through a one-step in situ hydrothermal method. The electrode polarization and reversibility have been improved by N-doped graphene with a three-dimensional conductive network structure, which contributes to notable electrochemical performance.

As one-dimensional nanomaterials, CNTs with perfectly connected hexagonal structures have excellent mechanical, electrical and chemical properties. For decades, with the in-depth research of CNTs and nanomaterials, CNTs have played a significant role in lithium-ion batteries. The composite electrode LFP/C/CNTs was reported by Huynh et al. [38]. The addition of CNTs into electrode composites improved the electrochemical behaviour by enhancing the electron and Li^+ transportation. D_{Li} increased with increasing CNT content in the composite electrode. In contrast, the LFP/C/10% CNTs presented higher retention capacity and rate capability than the composite without CNTs.

One-dimensional CNTs and two-dimensional graphene sheets can form effectively interconnected conductive networks due to their interwoven properties. Interestingly, only a few studies have focused on the incorporation of graphene and CNTs into $LiFePO_4$ [39-40]. Graphene and CNT co-modified $LiFePO_4$ cathode materials were synthesized via a hydrothermal method [40]. The combination of graphene and CNTs effectively constructed a three-dimensional conductive network, which offered highly conductive pathways for electron transfer and favoured the infiltration of electrolytes. Consequently, the significantly enhanced electrochemical activity of $LiFePO_4$ was observed.

3.1.2 Organic carbon materials

Most research is aimed at organic carbon material coatings on $LiFePO_4$ [7, 41]. The organic carbon material coating may improve the charge transfer at the LiFePO4/electrolyte interface and adapt to the volume change in the cathode material during cycling. To achieve even carbon coating, Xi and Lu [42] adopted sources and polyvinyl alcohol (PVA) as the carbon sources. As expected, the two different carbon sources were proven to be effective for improving the electrochemical performance of $LiFePO_4$ prepared under a low calcination temperature (650 °C) and short calcination time (4 h). Finally, the $LiFePO_4$/carbon composite with an approximately 2.7-nm-thick PVA coating showed high discharge capacities of 145 and 140 mA h g^{-1} at 5 C and 10 C, respectively.

PAni is a polymer compound that can have electrical conductivity and electrochemical properties after being doped. The electroactivity of PAni originates from the P-electron conjugated structure in the molecular chain. Recently, the PAni-coated $LiFePO_4$ compound was prepared through a solvothermal route [43]. In detail, Raman spectroscopy verified that the $LiFePO_4$ surface might chemically react with the structural conjugation of PAni. Additionally, the low charge transfer resistance (R_{ct}) values of 14 Ω cm^2 for $LiFePO_4$/PAni benefited the electron transfer velocity. As a consequence, the poor ionic and electronic conductivities of $LiFePO_4$ were effectively overcome.

Table 1 displays the electrochemical performance of $LiFePO_4$ with various (organic and inorganic) carbon material coatings.

Table 1. Electrochemical performance of $LiFePO_4$ with various carbon materials

Carbon material categories	**Carbon materials**	**Methods**	**Electrochemical properties**	**Ref.**
Inorganic carbon materials	Graphene	Hydrothermal	Discharge capacity: 93.6 mA h g^{-1}, 0.5 C, -30 °C D_{Li}: 2.15×10^{-13} cm^2 s^{-1}, -30 °C	[36]
	N-doped graphene	One-step in situ hydrothermal	First discharge specific capacity: 166.6 mA h g^{-1}, 0.2 C Discharge specific capacity: 125 mA h g^{-1}, 5 C R_{ct}: 58.6 Ω	[37]
	C/CNTs	Hydrothermal	D_{Li}: 4.80×10^{-11} cm^2 s^{-1} Specific capacity: 190 mA h g^{-1}, 0.1 C, after 200 cycles	[38]
	Graphene/CNTs	Hydrothermal	Initial discharge capacity: 168.4 mA h g^{-1}, 0.1 C Initial discharge capacity: 103.7 mA h g^{-1}, 40 C R_{ct}: 20.984 Ω D_{Li}: 5.744×10^{-11} cm^2 s^{-1}	[40]
Organic carbon materials	Glucose	Sol-gel and hydrothermal	Discharge capacity: 126 mA h g^{-1}, 0.2C Discharge capacity: 70 mA h g^{-1}, 3C Capacity retention: >97.5%, 0.5C, after 100 cycles	[7]
	Poly-acrylonitrile block polymethyl methacrylate	Carbothermal reduction	Initial discharge capacity: 165.3 mA h g^{-1}, 0.2C Reversible capacity: 78.9 mA h g^{-1}, 30C Capacity retention: 98%, 0.2C, 100 cycles	[41]
	PVA	Solid-state	Discharge capacity: 145 mA h g^{-1}, 5 C 140 mA h g^{-1}, 10 C	[42]
	PAni	Solvothermal	R_{ct}: 14 Ω cm^2	[43]

3.2 Metals

Although a conductive carbon coating can accelerate the electron rate and control the particle size of $LiFePO_4$, this approach results in problems related to the reduced energy density of $LiFePO_4$ due to the depressed tap density from the introduction of a lower tap density and non-active carbon material. Thus, an alternative method is metal or metal oxide coating. Metal or metal oxide coatings can guarantee the electron density of $LiFePO_4$ without decreasing the energy density and generate electron channels in the outer layer of the $LiFePO_4$ to facilitate the electron transfer rate.

In general, metal additives contain Ag [44], Cu [45] and Ga [46]. Both Cu and carbon have been added to coat $LiFePO_4$ by a carbothermal reduction process [45]. Cu distributed among the composites and homogeneous and tight carbon layers was detected by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which refined the particle size from 100-200 nm and increased the electron conductivity of $LiFePO_4$. Hence, the as-synthesized compound displayed prominent cycling ability and rate capability. Although Cu with high conductivity can improve the electrochemical dynamics for $LiFePO_4$, Cu is readily oxidized due to the decomposition of the electrolyte during discharge, which creates a potential barrier that prevents the release of Li^+ from the electrodes. Thus, the electrochemical performance of $LiFePO_4$ may decrease.

As far as we know, Ag has stable chemical properties, high ductility, and good thermal and electrical conductivity. On one hand, Ag speeds up the electron transfer and reduces the heat produced by limiting untoward reactions between electrolyte and electrode. In addition, Ag is less reductive than hydrogen, and it is difficult to react with HF to replace hydrogen, which helps protect the material. This can be applied to enhance the performance for cathode materials, such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ [47]. Similarly, Ag has been employed as a coating material to increase the electrical conductivity of $LiFePO_4$ [44]. Highly conductive Ag scattered onto the surfaces of $LiFePO_4$ improved the electronic conductivity and decreased the polarization and resistance of lithium-ion batteries. In the case of the Ag coating, Ag@$LiFePO_4$ exhibited superior cycling life and rate capabilities with 94 mA h g^{-1} at 5 C.

Ga shows a low melting point, a high boiling point and excellent electrical conductivity. Yi et al. [46] investigated Ga-coated $LiFePO_4$@C cathode materials. In their work, the carbon and Ga coating layers were approximately 2.3 nm and 3 nm, respectively. The growth of Ga made the conductive layer denser and more complete, which improved the conductivity and protected the electrode from corrosion when transporting electrons. Additionally, the electron conduction between sample particles can be greatly enhanced due to the presence of Ga coating on the particle surface, and the contact resistance between sample particles can be reduced, which optimizes the electrochemical performance of the cathode materials. Metal particles are difficult to homogeneously attach on $LiFePO_4$ surfaces. To overcome this issue, it is considered significant to decorate $LiFePO_4$ with both carbon and metal particles. Furthermore, Ga and Ag are expensive and not suitable for large-scale industrial applications.

Table 2 suggests the electrochemical performance of $LiFePO_4$ with a metal coating.

Table 2. Electrochemical performance of $LiFePO_4$ with metal coatings

Metals	**Methods**	**Electrochemical properties**		**Ref.**
		Before coating	**After coating**	
Ag	Solid-state	Discharge specific capacity: 52 mA h g^{-1}, 5 C	Discharge specific capacity: 94 mA h g^{-1}, 5 C	[44]

Cu	Carbothermal reduction	Initial discharge capacity: 157.3 mA h g^{-1}, 0.1 C Capacity retention: 91.7%, 0.5 C, 200 cycles	Initial discharge capacity: 160.7 mA h g^{-1}, 0.1 C Capacity retention: 98.6%, 0.5 C, 200 cycles	[45]
Ga	Hydrothermal and ultrasonic dispersion	Discharge capacity: 114.5 mA h g^{-1}, Capacity retention: 95.84%, 1 C, 100 cycles	Discharge capacity: 152.6 mA h g^{-1}, Capacity retention: 98.77%, 1 C, 100 cycles	[46]

3.3 Metal oxides

As a stable and conductive coating material, metal oxides have become the research object. The stable effect of the metal oxide coating prevents the dissolution of the $LiFePO_4$ cathode material and inhibits the side reaction between electrode and electrolyte, which is attributed to the reduced irreversible capacity loss and lower Li^+ migration resistance. The metal oxide coating can suppress the structural degradation of $LiFePO_4$ during charging and discharging, which increases the rate capacity and cycle life of $LiFePO_4$. Most commonly, metal oxides deemed as coating materials involve ZnO [48], MnO_2 [49] and others (Cu_xO [32], TiO_2 [50], Al_2O_3 [51]). In this work, as examples, the recent advances in ZnO and MnO_x coatings on $LiFePO_4$ will be summarized.

ZnO is an oxide of zinc with a large band gap and exciton binding energy, high transparency and excellent luminescence performance at room temperature. As a large bandgap semiconductor material, ZnO with a high electronic conductivity provides good electrical contact on the surface of active electrode material particles and facilitates the rapid transfer of Li^+ and electrons. Chen et al. [48] recently revealed the improved electrochemical performance of $LiFePO_4$ through ZnO and C co-modification. The enhancement in cycling stability and capacity was derived from the enhanced electrical conductivity and minimized Li^+ diffusion path. In addition, the consecutive conductive layer was confirmed by TEM analysis. From the perspective of the additive amount of ZnO, a relatively high amount (3 wt%) of ZnO with decreased R_{ct} (102 Ω) was responsible for a greater initial discharge capacity (138.7 mAh g^{-1}) at 0.1 C and better capacity retention (94.8%) after 50 cycles at 0.1 C.

With high specific capacity, low cost and environmental friendliness, MnO_2 has been increasingly recognized as an active electrode material. MnO_2 is also used as a coating material to improve the electrochemical properties of cathode materials. However, its low conductivity largely limits its application. With respect to this problem, the electrical conductivity can be improved by incorporating nanostructured MnO_2 into carbonaceous materials, which offers high electroactive surface areas and credible electronic connections. The Mn_xO/C co-coated $LiFePO_4$ was synthesized [49]. The research found that Mn_xO/C was closely adhered to $LiFePO_4$ with a significant increase in number of electroactive regions. Consequently, Mn_xO/C co-coated $LiFePO_4$ showed smaller polarization with a 0.2-V redox-potential separation and better electrochemical kinetics. Finally, the rate capability and cyclic stability of $LiFePO_4$ were remarkably improved.

The electrochemical properties of metal-oxide-coated $LiFePO_4$ are listed in Table 3.

Table 3. Electrochemical performance of $LiFePO_4$ with metal oxide coatings

Metal oxides	**Methods**	**Electrochemical properties**		**Ref.**
		Before coating	**After coating**	
ZnO	Inorganic-based hydrothermal	Discharge capacity: 105.5 mA h g^{-1}, Capacity retention: 85.2%, 0.1 C, 50 cycles	Discharge capacity: 131.5 mA h g^{-1}, Capacity retention: 94.8%, 0.1 C, 50 cycles	[48]
Mn_xO	Sol-gel	Initial discharge capacity: 141.2 mA h g^{-1}, Capacity retention: 92%, 1 C, 100 cycles	Initial discharge capacity: 151.4 mA h g^{-1}, Capacity retention: 96.6%, 1 C, 100 cycles	[49]
Cu/Cu_xO	Magnetron Sputtering	R_{ct}: 889 Ω, 2 C, after 150 cycles, 25 °C	R_{ct}: 299.1 Ω, 2 C, after 150 cycles, 25 °C	[32]
TiO_2	Wet chemical	Initial capacity: 127.4 mA h g^{-1}, 0.1 C	Initial capacity: 165.3 mA h g^{-1}, 0.1 C	[50]
Al_2O_3		Initial pecifific discharge capacity → Final pecifific discharge capacity: 84.2→83.2 mA h g^{-1}, 10 C, 300 cycles D_{Li}: 4.089×10^{-13} cm^2 s^{-1}	Initial pecifific discharge capacity → Final pecififc discharge capacity: 85.1→86.1 mA h g^{-1} , 10 C, 300 cycles D_{Li}: 6.908×10^{-13} cm^2 s^{-1}	[51]

3.4 Solid electrolytes and ion conductive materials

$LiFePO_4$ is a typical ionic mixing conductor. The desirable surface coating for $LiFePO_4$ should be an ionic and electronic conductor. In addition, the electrodes are protected from HF corrosion. Solid electrolyte materials have high ionic conductivity at room temperature. Therefore, they are considered very attractive cathode coating materials. Due to the high ionic conductivity of these materials, they are expected to optimize the charge transfer at the cathode/electrolyte interface, which improves the electrochemical performance, especially at high C rates. For better electrochemical performance, ionic conductive materials and solid electrolyte coatings have been applied to $LiFePO_4$. Common ionic conductive materials and mainstream solid electrolytes contain $GdPO_4$ [52], $Li_7La_3Zr_2O_{12}$ (LLZO) [53], $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) [54], etc.

Li's group focused on the ionic conductor $GdPO_4$ and C co-coated $LiFePO_4$ by the hydrothermal-assisted solid-phase method [52]. The facilitated electrochemical reaction between the $LiFePO_4$ particle interface and the electrolyte was ascribed to the smaller nanoparticles and more even dispersibility via $GdPO_4$ and C co-coating. Then, the ionic and electronic conductivity of $LiFePO_4$ was improved. In addition, the coating layer promoted the structural stability of $LiFePO_4$ nanoparticles in electrolytes. Consequently, the capacity retention, reversibility and exchange current density of $LiFePO_4$ significantly improved.

An Al-doped LLZO and carbon co-coated $LiFePO_4$ composite was studied by Bai et al. [53]. The LLZO fast ion conductor has good ion conductivity. Specifically, Al-doped LLZO decreased the Li^+ diffusion activation energy in LLZO, which is beneficial to the Li^+ rapid migration during the charging and discharging process and Li^+ conductivity of LLZO. The experimental results demonstrated that the solid electrolyte coating could inhibit the side reaction between the electrode and electrolyte, stabilize the olivine structure of $LiFePO_4$ and accelerate the diffusion of Li^+ at the electrode/electrolyte interface. Consequently, the amendatory cycling stability and high rate capability of $LiFePO_4$ were observed.

3.5 Cathode and anode materials

For decades, research on cathode and anode materials as coating additives has been performed because of their many advantages [55-56]. In particular, the added cathode and anode electrode materials have a stable structure, and they are coated on the original electrode material as a physical barrier to inhibit the detrimental side reactions between electrolyte and active substance; then, the electrochemical performance is optimized. For example, $Li_4V_2Mn(PO_4)_4$ as a cathode has a three-dimensional Li^+ diffusion channel, a high theoretical capacity and a stable structure at high operating voltage. Hence, $Li_4V_2Mn(PO_4)_4$ was used for the surface modification of Li-rich Mn-based cathode materials for lithium-ion batteries [56]. Experimental and theoretical results showed that $Li_4V_2Mn(PO_4)_4$ could reduce the content of residual Li compounds on the surface and impede the dissolution of transition metals. Simultaneously, it could diminish the Li^+ diffusion energy barrier and offer an effective diffusion method.

In recent years, the layered transition metal dichalogenide MoS_x has raised concerns due to its fantastic chemical and physical characteristics. The investigations suggested MoS_2 as an electrode candidate for lithium-ion batteries. In Hu's study [55], core-shell structured $LiFePO_4$ was successfully prepared by MoS_x surface coating, where MoS_x acted as the shell. Surprisingly, the surface-modified $LiFePO_4$ had a dramatic specific capacity of 228 mA h g^-1, which was much higher than its theoretical capacity. The exceeding capacity came from Li^+ intercalated/deintercalated through the MoS_x layers at voltages of 2.0-3.8 V. Meanwhile, MoS_x modification reinforced the structural stability of $LiFePO_4$. Therefore, superior electrochemical properties were achieved.

4. CONCLUSIONS AND FUTURE OUTLOOK

With its advantages of a long cycle life, high safety and low cost, $LiFePO_4$ cathodes are rapidly developing in the electric vehicle power battery and energy storage battery markets. Unfortunately, the poor conductivity and low Li^+ diffusion velocity restrict the comprehensive application of $LiFePO_4$ cathodes. The performance for $LiFePO_4$ has been enhanced through surface coating, ion doping and particle size reduction strategies. Based on previous literature, this paper systematically summarizes the role of surface coatings on $LiFePO_4$ materials and the main types of surface coating materials. The main surface coating materials include carbon, metals, metal oxides, solid electrolytes, ion conductive materials, cathodes and anode materials. As a surface modification technology, the surface-coated $LiFePO_4$ material delivers good reversibility and high rate performance. However, surface coatings need further research, whether in lithium-ion batteries or other types of batteries. These discussions provide guidance for the critical necessity and proper development direction of lithium-ion batteries and other types of batteries with high energy density, high safety, long cycle life and low cost.

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References

1. M. Hirooka, T. Sekiya, Y. Omomo, M. Yamada, H. Katayama, T. Okumura, Y. Yamada and K. Ariyoshi, *J. Power Sources*, 463 (2020) 228127.
2. H. H. Ryu, B. Namkoong, J. H. Kim, I. Belharouak, C. S. Yoon and Y-K. Sun, *ACS Energy Lett.*, 6 (2021) 2726.
3. J. P. Tian, R. Xiong, W.X. Shen and J. H. Lu, *Applied Energy*, 291 (2021) 116812.
4. R. Wu, T. Cao, H. Liu, X. Cheng, X. Liu and Y. Zhang, *ACS Appl. Mater. Interfaces*, 14 (2022) 925524.
5. M. Mock, M. Bianchini, F. Fauth, K. Albe and S. Sicolo, *J. Mater. Chem. A*, 9 (2021) 14928.
6. K. Nakajima, F. L. Souza, A. L. M. Freitas, A. Thron and R. H. R. Castro, *Chem. Mater.*, 33 (2021) 3915.
7. M. A. M. M. Alsamet, E. Burgaz, *Electrochim. Acta*, 367 (2021) 137530.
8. S. Bibi, A. Khan, S. Khan, A. Ahmad, S. S. Shah, M. Siddiq, A. Iqbal and A. A. Al-Kahtani, *Int J Energy Res.*, 46 (2021) 810.
9. X. C. Wu, M. Meledina, H. Tempel, H. Kungl, J. Mayer and R.- A. Eich, *J. Power Sources*, 450 (2020) 227726.
10. C. Q. Shen, G. R. Li, L. Liu, P. F. Li, H. Xu, H. S. Hu and L. B. Wang, *J. Power Sources*, 496 (2021) 229759.
11. T. T. Xu, J. Y. Su, E. Ha and L. Y. Wang, *Mater. Lett.*, 274 (2020) 128006.
12. Y. Li, L. Wang, F. Liang, Y. C. Yao and K. Y. Zhang, *J. Alloys Compd.*, 880 (2021) 160560.
13. Y. C. Li, Y. P. Zhang, J. J. Ma, L. Wang, X. B. Li, E. Q. Zhao, S. M. Fan, G. R. Xu, S. T. Yang and C. C. Yang, *J. Electrochem. Soc.*, 166 (2019) A410.
14. B. Q. Zhang, S. Z. Wang, L. H. Liu, Y. Li and J. Q. Yang, *Materials*, 15 (2022) 4738.
15. W. C. Chien, Y. R. Li, S. H. Wu, Y. S. Wu, Z. H. Wu, Y. J. J. Li and C. C. Yang, *Adv Powder Technol.*, 31 (2020) 4541.
16. S. Khan, R. P. Raj, L. George, G. S. K. Kannangara, A. Milev, U. V. Varadaraju, and P. Selvam, *ChemistryOpen*, 9(2020) 23.
17. G. Geng, Y. Li, X. Shang, B. Xing, K. Zhou, Z. Shang, L. Yang, G. Xu and J. Hao, *Int. J. Electrochem. Sci.*, 17 (2022) 220722.
18. Y. Liu, Y. J. Gu, G. Y. Luo, Z. L. Chen, F. Z. Wu, X. Y. Dai, Y. Mai and J. Q. Li, *Ceram. Int.*, 46 (2020) 14857.
19. Z. Y. Chen, Q. F. Zhao, M. Xu, L. J. Li, J. F. Duan, H. L. Zhu, *Electrochim. Acta*, 186 (2015) 117.
20. J. K. Kim, S. M. Jeong, *Appl. Surf. Sci.*, 505 (2020) 144630.
21. J. Y. Liua, X. R. Lin, T. L. Han, X. X. Li, C. P. Gu, J. J. Li, *Appl. Surf. Sci.*, 459 (2018) 233.
22. M. G. Moustafa, M. M.S. Sanad, *J. Alloys Compd.*, 903 (2022) 163910.
23. Z. P. Ma, Y. S. Peng, G. L. Wang, Y. Q. Fan, J. J. Song, T. T. Liu, X. J. Qin, G. G. Shao, *Electrochim. Acta*, 156 (2015) 77.
24. C. C. Yang, J. H. Jang, J. R. Jiang, *Appl. Energy,* 162 (2016) 1419.
25. H. Goktepe, H. Sahan, S. Patat, *Int. J. Hydrog. Energy*, 41 (2016) 9774.
26. P. Handel, G. Fauler, K. Kapper, M. Schmuck, C. Stangl, R. Fischer, F. Uhlig, S. Koller, *J. Power Sources*, 267 (2014) 255.
27. T. Kawamura, S. Okada, J. Yamaki, *J. Power Sources*, 156 (2006) 547.

28. M. Koltypin, D. Aurbach, L. D. Nazar and B. Ellis, *Electrochem. Solid-State Lett.*, 10 (2007) A40.
29. M. Koltypin, D. Aurbach, L. Nazar, B. Ellis, *J. Power Sources*, 174 (2007) 1241.
30. G. Wu, T. T. Jiang, X. H. Tian, Y. B. Zhu, Y. K. Zhou, *Int. J. Electrochem. Sci.*, 13 (2018) 8006.
31. X. M. Cui, D. W. Yi, N. L. Li, L. Zhang, X. F. Zhang, and D. Y. Yang, *Energ. Fuel.*, 34 (2020) 7600.
32. W. Y. Yang, Y. Chen, X. H. Peng, Y. B. Lin, J. X. Li, Z. S. Hong, G. G. Xu, and Z. G. Huang, *ACS Appl. Energy Mater.*, 2 (2019) 4652.
33. C. Wang, X. L. Yuan, H. Y. Tan, S. F. Jian, Z. T. Ma, J. J. Zhao, X. W. Wang, D. P. Chen, and Y. F. Dong, *Coatings*, 11 (2021) 1137.
34. J-K. Kim, S. M. Jeong, *Appl. Surf. Sci.*, 505 (2020) 144630.
35. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *SCIENCE*, 306 (2004) 666.
36. B. F. Zhang, Y. L. Xu, J. Wang, X. N. Ma, W. Q. Hou, X. Xue, *Electrochim. Acta*, 368 (2021) 137575.
37. G. Y. Luo, Y. J. Gu, Y. Liu, Z. L. Chen, Y. I . Huo, F. Z. Wu, Y. Mai, X. Y. Dai, Y. Li, *Ceram. Int.*, 47 (2021) 11332.
38. L. T. N.Huynh, T. T. D. Tran, H. H. A. Nguyen, T. T. T. Nguyen, V. M. Tran, A. Grag, M. L. P. Le, *J Solid State Electrochem.*, 22 (2018) 2247.
39. Y. K. Liu, H. Zhang,Z. Huang, Q. Wang, M. Y. Guo, Mi. Q. Zhao, D. Y. Zhang, J. G. Wang, P. He, X. Y. Liu, M. Terrones, Y. Q. Wang, *J. Alloys Compd.*, 905 (2022) 164205.
40. Y. T. Chen, H. Y. Zhang, Y. M. Chen, G. Qin, X. L. Lei, L. Y. Liu, *Mater. Sci. Forum*, 913 (2018) 818.
41. M. Shi, R. W. Li, Y. L. Liu, *J. Alloys Compd.*, 854 (2021) 157162.
42. Y. M. Xi and Y. C. Lu, *Ind. Eng. Chem. Res.*, 59 (2020) 3549.
43. W. S. Fagundes, F. F. S. Xavier, L. K. Santana, M. E. Azevedo, S. C. Canobre, F. A. Amaral, *Mater. Res.*, 22 (2019) e20180566.
44. E. C. Meng, M. Zhang, Y. Hu, F. L. Gong, L. S. Zhang, F. Liang, *Electrochim. Acta*, 265 (2018) 160.
45. M. Y. Zhu, L. F. Cheng, Y. Liu, W. X. Li, P. F. Hu, H. M. Jin, Y. M. Hu, Y. Li, *Ceram. Int.*, 44 (2018) 12106.
46. D. Yi, X. Cui,N. Li, L. Zhang, D. Yang, *ACS Omega*, 5 (2020) 9752.
47. H. L. Sun, Y. F. Zhang, W. Li, D. Zhang, Q. J. Wang, B. Wang, *Electrochim. Acta*, 327 (2019) 135054.
48. X. H. Chen, Y. Li, J. Wang, *Nanomaterials*, 11 (2021) 12.
49. S. J. Kim, J. H. Cho, K. Y. Lee, B. W. Cho, K. Y. Chung, J. Y. Kim, Bull. Korean *Chem. Soc.*, 40 (2019) 317.
50. J. Y. Shi, X. Q. Zhang, X. K. Zhang, Y. Xiang, *J. Alloys Compd.*, 750 (2018) 139.
51. X. K. Huang, K. Chen, Y. Z. Liu, *Mater. Res. Express*, 6 (2018) 015511.
52. Y. Li, J. Wang, H. X. Huang, J. Wang, M. Zhang, MM. Liang, *Adv Powder Technol.*, 30 (2019) 1442.
53. Y. X. Bai, J. Zhang, Y. B. Yang, R. Yang, Y. L. Yan, J. Wang, *J. Alloys Compd.*, 843 (2020) 154915.
54. C. C. Yang, J. R. Jiang, C. Karuppiah, J. H. Jang,Z. H. Wu, R. Jose, S. j. J. Lue, *J. Alloys Compd.*, 765 (2018) 800.
55. L. H. Hua, P. Kumar, *J. Alloys Compd.*, 872 (2021) 159718.
56. S. Q. Yang, P. B. Wang, H. X. Wei, L. B. Tang, X. H. Zhang, Z. J. He, Y. J. Li, H. Tong, J. C. Zheng, *Nano Energy,* 63 (2019) 103889