Progress in the Application of $LiMnPO_4$ Nanomaterials in Lithium-ion Battery Cathode

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Abstract. Lithium-ion batteries (LIBs) have become vital in today's energy storage systems, especially for electric cars and portable gadgets. High energy density, extended cycle life, and quick charging times are features of lithium batteries. Compared to conventional batteries, they are lightweight, ecologically benign, and have a low self-discharge rate. $LiMnPO_4$ nanomaterials have garnered significant interest among various cathode materials due to their superior thermal stability, safety, and high operating voltage. The main topics of this paper are the structural characteristics, production techniques, and performance improvements of $LiMnPO_4$ nanoparticles as LIBs cathodes. The basic operating principles of LIBs were covered in this article, with particular attention paid to the redox reactions occurring at the electrodes, the unique olivine structure of $LiMnPO_4$, and how these factors affect electrochemical performance. The efficiency of many synthesis methods, such as spray pyrolysis, sol-gel, solid-state, hydrothermal, and solvothermal processes, in yielding superior $LiMnPO_4$ nanoparticles is assessed. Additionally, surface modifications through ion doping and carbon coating are reviewed to highlight their roles in enhancing conductivity and stability. This article aims to provide ideas for developing high-performance $LiMnPO_4$ cathode materials to affect LIBs' development positively. This article aims to provide ideas for developing high-performance LiMnPO4 cathode materials to influence LIBs' development positively.

Keywords: Lithium-ion batteries, $LiMnPO_4$, cathode.

1. Introduction

These days, LIBs are essential for modern energy storage. They are perfect for various applications because of their high energy density, extended cycle life, and low self-discharge rates [1]. The materials used for LIBs electrodes significantly impact their performance, and the cathode material is a critical factor in deciding the overall safety and efficiency of the battery.

The cathode in LIBs stores and releases lithium ions during charge and discharge cycles. Typically, it is composed of lithium metal oxides like $LiCoO_2$ or $LiFePO_4$. The anode, typically composed of graphite, holds lithium ions during charging and releases them during discharging. Lithium ions can move between the anode and cathode through the separator, a microporous membrane commonly composed of polyethylene or polypropylene that inhibits electrical short circuits. The liquid medium known as the electrolyte facilitates the transfer of lithium ions between the electrodes and is typically composed of lithium salts such as $LiPF_6$ in organic solvents. Together, these elements allow LIBs to store and release energy.

$LiMnPO_4$ nanomaterials have emerged as a promising cathode material due to their high thermal stability, safety, and high operating voltage (4.1V) [2, 3]. These attributions make $LiMnPO_4$ nanomaterials an attractive alternative to conventional cathode materials like $LiCoO_2$ and $LiFePO_4$. The olivine structure of $LiMnPO_4$, characterized by its orthorhombic crystal system, facilitates stable Li^+ intercalation/de-intercalation processes, essential for maintaining high electrochemical performance over extended cycles. In addition, $LiMnPO_4$ nanomaterials in LIBs also have the advantages of high safety, long life, good high-temperature performance, environmentally friendly and non-polluting, large capacity, and no memory effect, which make them have a wide range of applications in the field of new energy vehicles, energy storage systems, and other areas.

This review aims to provide a review of $LiMnPO_4$ nanomaterials in the context of LIBs cathodes and have a role in guiding the future research of $LiMnPO_4$ nanomaterials.

2. Working Mechanism of LIBs

The four primary parts of a Li-ion battery are the cathode, anode, electrolyte, and separator located in the middle of the battery. Figure 1 illustrates the Li-ion battery's operation [4]. The basic principles of Li-ion batteries are reduction and oxidation reactions that occur at the cathode or anode through electrochemical redox reactions. An electrolyte switches its function as an anode or a cathode during the charging or discharging period. Generally, a cathode is where oxidation reactions (losing electrons) happen during the charging period, and reduction reactions (gaining electrons) occur during the discharging period. However, an anode is where oxidation reactions (losing electrons) happen during the discharging period, and reduction reactions (gaining electrons) occur during the charging period.

The following is a description of how a Li-ion cell operates. Electrons are removed from the cathode material and moved to the anode via the external circuit during the charging phase. Li^+ is taken out of the cathode in the interim [5]. They enter the anode after going through the separator and electrolyte. Thus, as Figure 1 shows, current travels from the anode to the cathode. Reverse reactions happen during the discharge phase. The Li^+ travels from the anode to the cathode via the electrolyte and separator. In contrast, the electrons move from the anode to the cathode through the external circuit and electrical appliances. So, the current flow is from the cathode to the anode. The anode's Li electric potential is significantly higher than the cathode's during the charging phase. Consequently, the cell converts and stores the electrical energy into chemical energy. During the discharging phase, this process is reversed, converting the chemical energy in the cell into electrical energy consumed by electrical equipment [6].

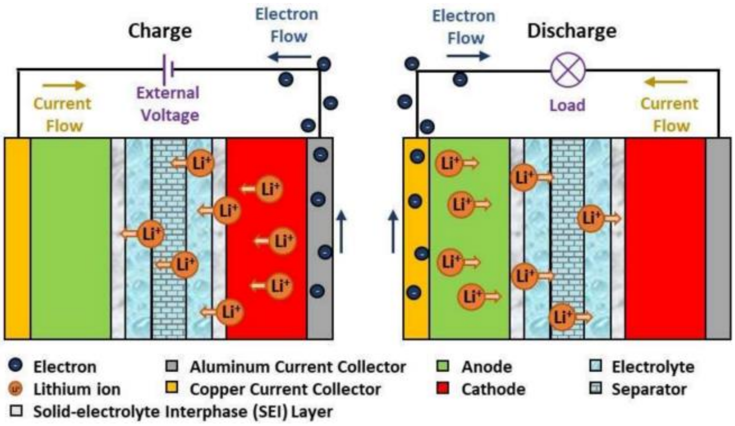

Figure 1. The working mechanism of LIBs [1]

3. Structure of $LiMnPO_4$

Figure 2 illustrates the crystal structure of $LiMPO_4$ cathode materials, which is based on a distorted hexagonal close-packed (hcp) oxygen framework. Half of the available octahedral sites in this structure are occupied by lithium and manganese ions, while phosphorus ions occupy one-eighth of the tetrahedral sites. Li and Mn ions are arranged in octahedral positions, while P ions are positioned in tetrahedral sites in the orthorhombic olivine structure that defines $LiMnPO_4$. The 4c site is occupied by the oxygen atoms O_1 and O_2, O_3 occupies the 8d site, and Mn and P ions occupy the 4c site. Lithium has a Wyckoff position of 4a (0,0,0). These materials' general chemical formula, $LiMPO_4$, verifies their olivine structure. The +1 charge of lithium and the +2 charge of manganese balance the -3 charge of the phosphorus ions. The material changes to $MnPO_4$ when the lithium is removed. Here, the Mn atom is centrally coordinated inside an octahedral configuration of six oxygen atoms, or MnO_6. The normal octahedral Oh symmetry is reduced to Cs symmetry by the distortion of these MnO_6 octahedra. The octahedral MnO_6 and the tetrahedral phosphate groups (PO_4) form the three-dimensional structure, which shares oxygen corners by sharing two edges with LiO_6 octahedra and a standard edge with one MnO_6 octahedron. The tetrahedral PO_4 units link adjacent MnO_6 octahedral layers. The octahedral channels include zigzag-like arrangements of lithium ions. From a crystallographic perspective, this structure is a part of the orthorhombic crystal system's Pmnb space group [2].

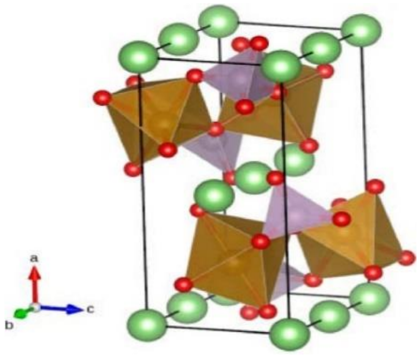

Figure 2. The structure of $LiMPO_4$ [2]

4. Synthesis Methods of $LiMnPO_4$ Nanomaterials

4.1. Sol-gel Method

Low temperatures are used in the sol-gel process to dissolve raw ingredients into water or ethanol. It aggressively stirs to create a uniform sol, a stable colloidal suspension of solid particles in a solvent [2]. The gel (a relatively thick gel-like material generated owing to the gelation of the sol consisting of porous interconnecting stiff skeletal colloidal particles [2]) is formed [1] by adding chelating chemicals, such as citric acid, oxalic acid, etc., and raising the temperature. Following that, a high-temperature treatment eliminates all liquids from the pores' surfaces, which reduces the quantity and connectivity of pores through a process called densification [7].

Esmezjan et al. [8] created a carbon-coated $LiMnPO_4$ ($LiMnPO_4/C$) cathode material using the sol-gel technique. They employed raw materials from ammonium dihydrogen phosphate, manganese acetate tetrahydrate, and lithium acetate dihydrate. The spherical nature of the particles on the surface was revealed using scanning electron microscopy (SEM). They range in size from 100 to 200 nm, with a consistent distribution of diameters. According to electrochemical performance testing, this material can charge at 135 mAh/g and has a voltage plateau of about 4.1V.

$LiMnPO_4/C$ material was prepared by Zhong et al. [9] using a sol-gel technique with citric acid. They suggested that in addition to acting as a chelating agent that aids particle size reduction, citric acid also functions as a carbon source. Carbon monoxide from citric acid is produced during calcination, which helps to keep Mn^{2+} stable. The outcomes demonstrated that the sol-gel process obtained good electrochemical reversibility. When $LiMnPO_4/C$ was synthesized for 10 hours at 500°C, it showed a maximum initial discharge capacity of 122.6 mAh/g and continued to hold this capacity for 30 cycles at a rate of 0.05 C.

4.2. Solid-state Method

A classic and somewhat straightforward synthesis technique, the solid-state reaction usually requires two heating phases. Materials are heated to between 300 and 400°C and undergo a second treatment at 600 to 800°C. This method is widely adopted in advanced technologies due to its simplicity and feasibility for large-scale production. However, the requirement for high temperatures increases costs and often results in larger product sizes. The solid-state reaction is particularly suited for large-scale production, making it ideal for industrial applications. High pressure and temperature parameters are necessary for this synthesis method. However, the lengthy processes that need repeated calcination and grinding often result in bigger particles, which might impair electrochemical performance [1, 2].

Hu et al. [10] synthesized a composite material ($LiMn_{0.9}Fe_{0.09}Mg_{0.01}PO_4/C$) using lithium dihydrogen phosphate, manganese acetate tetrahydrate, oxalic acid, ferrous oxalate, and magnesium acetate tetrahydrate as the primary raw materials through the solid-state synthesis method. High discharge capacity and superior cycle performance are demonstrated by this composite material at both room temperature and higher temperatures. With a capacity deterioration of less than 1%, the discharge capacity was steady at 135mAh/g over 120 charge-discharge cycles at 50°C and one °C. The results of the trials demonstrated that co-doping with Fe and Mg efficiently prevented Mn^{3+} ions from dissolving, which improved the material's high-rate performance and cycle stability at high temperatures and resulted in a more stable olivine structure.

4.3. Hydrothermal Method

Hydrothermal synthesis is a wet chemical method conducted in aqueous or alcoholic solutions at temperatures above boiling points. These techniques are advantageous due to their simplicity, ability to produce uniform and controlled morphology, and cost-effectiveness. In these processes, water acts as the reaction medium, and the starting materials are placed in a Teflon-lined autoclave. The autoclave is heated above 100°C, generating vapor pressure in a closed system. Consequently, the hydrothermal method is a straightforward, efficient, and economical wet process that yields powders with high homogeneity and purity. Specifically, the hydrothermal method has been optimized for the production of $LiMnPO_4$ powders [2].

Priyadharsini et al. [11] combined lithium dihydrogen phosphate, manganese acetate tetrahydrate, and citric acid in polyethylene glycol 400 (PEG-400) solvent, stirring the mixture thoroughly. The resulting mixture was then transferred into an autoclave for hydrothermal synthesis to produce $LiMnPO_4$ powder. Post-synthesis, the powder underwent heat treatment at 400°C to enhance its purity and crystallinity. The synthesized product exhibited a rod-like structure with particle sizes ranging from 100 to 200nm.

4.4. Solvothermal Method

The solvothermal synthesis method operates in a manner similar to hydrothermal synthesis but employs an organic solvent, such as alcohol, instead of water as the reaction medium. This method involves placing the reactants in an autoclave, which is then heated to a temperature above the boiling point of the chosen solvent. Organic solvents can offer unique advantages, such as better solubility for specific precursors and the ability to produce materials with distinct properties. Like the hydrothermal method, solvothermal synthesis is relatively straightforward and cost-effective, requiring essential equipment such as an oven or autoclave. This method is beneficial for producing materials with controlled morphology and high purity, making it a versatile technique in the field of material science [2]. Yang synthesised $LiMnPO_4$ nanocomposites using Li_3PO_4 nanorods and $MnSO_4$-H_2O as starting materials by solvothermal method with a discharge capacity of 147 mAh/g [12].

4.5. Spray Pyrolysis Method

Spray pyrolysis is highly effective for generating fine particles from nano to micro sizes. In this technique, an atomizer transforms a precursor solution into droplets. These droplets undergo evaporation and decomposition, resulting in the formation of particles and films. The fundamental principle behind spray pyrolysis is continuously producing aerosols from the precursor solution via the atomizer. The essential steps in this method include preparing the precursor colloidal solution, generating and transporting the aerosol, and executing the synthesis process. Typically, the aerosol, which contains the precursor, is directed onto a heated substrate, forming well-crystallized and pure-phase fine particles [2].

5. Modification of $LiMnPO_4$ Nanomaterials

5.1. Ion Doping

Ion doping enhances the performance of materials by altering their structure. This process primarily involves doping at Li, Mn, and P sites, with Mn site doping being the most prevalent.

In Li site doping, ions with larger radii replace some of the Li^+ ions, thereby expanding the diffusion channel radius for Li^+, reducing charge transfer resistance, and improving the rate capability of the material. Compared to Li site doping, Mn site doping with metal ions such as Fe^{2+}, Co^{2+}, and Zn^{2+} can suppress the Jahn-Teller effect of Mn^{2+} and prevent the dissolution of Mn^{3+}, thereby significantly enhancing the material's electrochemical performance.

Research on P-site doping is less extensive. This method involves substituting a small amount of P with non-metal elements to induce minor changes in the anionic groups, thus widening the Li+ diffusion channels and lowering the energy barriers for Li^+ diffusion. Doping changes can improve the ionic and electronic conductivity of $LiMnPO_4$ materials, inhibit the Jahn-Teller phenomenon, and alter the material's grain size and internal transport characteristics. Regarding enhancing performance, Mn site doping outperforms Li and P site doping. Currently, elements used for doping include Zn, Cu, Mg, Ca, V, Ti, Zr, Fe, Co, Ni, and others. The type and amount of doping elements significantly influence the modification outcomes [1, 2]. Wang et al. [13] synthesized $LiMnPO_4$ materials doped with Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} using a solid-state method. Among these materials, the Fe-doped product exhibited the smallest particle size and the highest electrical conductivity, resulting in the best discharge capacity and rate performance.

5.2. Carbon Coating

Carbon coating can enhance the surface conductivity of $LiMnPO_4$ materials, enabling rapid electron transfer and making it a common and effective method for modifying $LiMnPO_4$. The improvement from carbon coating is primarily influenced by the type of carbon source, the amount used, and the uniformity of the coating. Recently, carbon nanotubes and graphene have been chosen as new carbon sources for modifying $LiMnPO_4$ materials due to their unique conductive properties.

Carbon surface modification substantially inhibits the growth of $LiMnPO_4$ particle size while simultaneously improving interparticle conductivity and shortening Li^+ ion diffusion routes. This enhances the material's rate capability and charge-discharge performance. When creating high-performance $LiMnPO_4$ cathode materials, choosing the right carbon source is essential. In addition to inorganic materials like acetylene black and Ketjen black, familiar organic carbon sources include glucose, sucrose, and cyclodextrin. Because of its superior chemical stability, elasticity, and conductivity, graphene is regarded as the perfect carbon covering for cathode material modification.

The carbon content in the material plays a vital role in enhancing the rate capability of $LiMnPO_4$. Previous studies [14] have shown that when the carbon mass fraction is 3.80%, the composite material's initial discharge capacity can reach 140mAh/g at 0.1 C. Under these conditions, the composite material exhibits optimal electrochemical performance. If the carbon content is too low, the $LiMnPO_4$ surface cannot be fully coated, while excessive carbon content can negatively affect the material's capacity.

6. Conclusion

Because of its excellent thermal stability, safety, and electrochemical characteristics, $LiMnPO_4$ nanoparticles have a lot of potential as cathodes for next-generation lithium-ion batteries. The current techniques for creating $LiMnPO_4$ nanomaterials, such as spray pyrolysis, hydrothermal, solid-phase, sol-gel, and hydrothermal processes, are compiled in this work. Furthermore, this work suggests two modification techniques, ion doping, and carbon coating, to enhance the characteristics of $LiMnPO_4$ and, therefore, the efficacy of LIBs.

However, the cycle life of $LiMnPO_4$ is shorter than that of materials such as $LiFePO_4$. This is mainly because the addition of manganese elements may lead to manganese leaching, which affects the cycling stability and capacity retention of the material. As the number of cycles increases, the capacity of lithium manganese phosphate will gradually decrease. Possible side reactions between lithium manganese phosphate and electrolyte will also further affect its charging and discharging performance, affecting the battery's charging and discharging efficiency and cycle life. More seriously, the stability of lithium manganese phosphate is relatively poor in high-temperature environments, and it is easy to lose capacity and life. This is a disadvantage for lithium-ion batteries operating at high temperatures.

Future research could focus on incorporating other transition metal ions and rare earth ions to alter the structure of LMP. This could significantly enhance its conductivity and the diffusion rates of lithium ions within the cathode material. Developing new methodologies and techniques to extend the cycle life and improve the high-temperature performance of LMP is crucial. This could involve advanced material engineering and better thermal management solutions. Researchers can tailor the crystal size and morphology by precisely controlling the synthesis parameters such as temperature and time. Creating nanostructures like nanorods and nanosheets can significantly boost the electrochemical performance of LMP.

$LiMnPO_4$, as a cathode material for lithium-ion batteries, holds significant potential for the future. With ongoing technological innovations and enhancements in performance, $LiMnPO_4$ is poised to find extensive applications in electric vehicles, energy storage systems, and consumer electronics.

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