LiMnPO$_4$: Review on Synthesis and Electrochemical Properties

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Abstract

The olivine structured mixed lithium-transition metal phosphates LiMPO$_4$ (M = Fe, Mn, Co) have attracted tremendous attention of many research teams worldwide as a promising cathode material for lithium batteries and for studying their magnetic and electrical properties. High energy density is required for mind- to large-scale batteries because the mounting spaces are quite small for vehicles and other energy storage applications. This constraint necessitates synthesis to yield high volumetric energy density and reliable battery performance. Development of eco-friendly, low cost and high energy density, LiMnPO$_4$ cathode material became attractive due to its high operating voltage, which can be located inside of the electrochemical stability window of conventional electrolyte solutions and it offers more safety features due to the presence of a strong P-O covalent bond. This review is an overview of current research activities on LiMnPO$_4$ cathodes and its carbon coating synthesized by various synthetic techniques.

Keywords

Synthesis, Properties, LiMnPO$_4$

1. Introduction

Since the pioneering work of Goodenough et al. [1], the Phospho-olivine LiMPO$_4$ compound (with M equal Fe, Mn, Co or Ni) have been recognized as a potential positive electrode material for used in lithium rechargeable batteries. This family of materials has numerous advantages over the layered rock salt oxides (e.g. LiCoO$_2$ and LiNiO$_2$) that are currently used in commercial batteries. Besides its high discharge capacity ($\approx$170 mA·h·g$^{-1}$), LiMPO$_4$ cathode material shows high stability during lithium extraction/insertion and does not deteriorate when

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used at moderately high temperatures. Recently, a lot of effort has been devoted to optimize LiFePO₄ material. In particular, particle minimization with intimate carbon contact resulted in almost the theoretical capacity at moderate current densities with LiFePO₄ cathode material [2]. Surprisingly, only a few papers indicate the applicability of LiMnPO₄ [3]-[5] and, the results remain controversial.

The origin of the different electrochemical activities of isostructural LiFePO₄ and LiMnPO₄ is not quite clear at the moment. Yamada et al. [3] suggested that the low electrochemical activity of LiMnPO₄ is due to slow kinetics and internal friction during lithium extraction/insertion. Akin et al. has recently performed a comparative structural study [6] of these two materials and found minute differences in the oxygen vibrations in the Li layer. Yet another important factor is the magnetism in these compounds [7]-[9]. The magnetic properties are determined by the magnetic moment and may thus reflect the potential differences within the LiMPO₄ family. Magnetism is therefore indirectly important for electrochemical properties as well.

Figure 1 presents the schematics of the LiMnPO₄ olivine structure. LiMnPO₄ has an olivine structure, where Mn and Li occupy octahedral 4c and 4a sites, and P atom is in 4c site, respectively. The O atoms are in a hexagonal close-packed arrangement. The MnO₆ octahedral is separated by PO₄ plain that leads to the significant reduction of the electrical conductivity of the material. It results in a poor rate capability and a slow utilization of Li ions in the olivine host structure. Therefore, similarly to LiFePO₄, the successful preparation of high performance LiMnPO₄ could be achieved through the preparation of the conductive composites of fine particles of this material. However, the current durability of LiMnPO₄ is orders-of-magnitude inferior to that of LiFePO₄ [10], which make the preparation of the high conductivity LiMnPO₄/C composites, more difficult than in the case of the lithium-iron phosphate.

In the olivine structures the magnetic ions occupy only the so-called M₂ site, i.e. the M₂⁺ ion sits in the center of MO₆ unit. Each MO₆ distorted octahedron is connected to four other MO₆ via vertices forming a layered network perpendicular to the crystal (100) direction. Successive M₂⁺ layers are separated by PO₄ tetrahedral and LiO₆ octahedral.

Only few routes synthesis for LiMnPO₄ has been proposed. Powder properties are strongly affected by the preparation technique. In this review, special attention is focused on obtaining LiMnPO₄.

2. Synthesis Method and Properties of LiMnPO₄

2.1. Solid-State Reaction

Some research groups have tried to use solid-state reactions to synthesize LiMnPO₄. The solid state reaction is a conventional synthesis method, which usually needs a two-step heating treatment, including the first firing in a temperature range of 300°C - 400°C and subsequent one between 600°C and 800°C. The solid state reaction method has been a developed technology and being used much frequently since it’s simple to synthesis and easy to make mass production. The need for high temperature unfortunately upgrades cost; what is more, the product size always cannot be small. So other measures are added to circumvent those problems to process olivine
phosphates, such as slighter temperatures or adding carbon. Table 1 shows the precursors used in the solid-state reaction of the resultant LiMnPO₄ and composites of this phase.

The effect of Fe₂⁺ substitutions was successfully employed by Martha et al. [11] to form a solid solution between olivine phases of Fe and Mn. A solid state method was employed for the preparation of such a LiMn₀.₈Fe₀.₂PO₄ phase along with 10 wt% carbon by ball milling before the heat treatment at 550 °C for 3 h in Ar atm. The olivine phase LiMn₀.₈Fe₀.₂PO₄ comprised 25 - 60 nm size particulates with ≈5 nm thick carbon coating on the surface. Yang et al. [12] reported the synthesis of Co doped LiMnP₀₄ (LiMn₀.₉₅Co₀.₅PO₄) by an oleic acid assisted approach. The source materials were initially ball milled before the heat treatment in N₂ atmosphere at various calcination temperatures.

The sample prepared at 600 °C performed better when compared to other temperature conditions and it showed discharge capacities of 103 and 144 mA·h·g⁻¹ for LiMnP₀₄ and LiMn₀.₉₅Co₀.₅PO₄ respectively at a 0.05 C rate between 2.5 and 4.5 V is using the CC-CV protocol. LiMnP₀₄ with off-stoichiometry (LiMn₀.₉₅P₀.₉₅O₄₋₅) was reported by Kan and Ceder [13] with a particle size of <50 nm. The preparation phase contains some impurity phases like Li₃PO₄ and Li₄P₂O₇; the concentration of those phases was totally less than 5% of native compound, hence the theoretical capacity of LiMnP₀₄ was assumed to be 162 mA·h·g⁻¹. To prepare Fe and Mg co-doped LiMnP₀₄ with 14 wt% of sucrose, a solid-state route has been adopted with subsequent ball milling for 6 h by Hu et al. [14] [15]. Four different synthesis temperatures, namely, 650 °C, 750 °C, 800 °C and 850 °C were studied. When the temperature exceeds 800 °C it leads to the formation of Fe₂P impurity during Fe substitution. Hence, 800 °C for 10 h was well suited to obtain the best performing single phase material. The final comprised ≈ 7.5 wt% carbon for all the three temperatures except 850 °C (~5.7 wt%). The electrochemical properties of C-LiMn₀.₈Fe₀.₁₋ₓMgxPO₄ where x = 0.01, 0.02 and 0.05 were evaluated using CC-CV mode at 4.5 V vs Li.

Capacity profiles increased with increasing synthesis temperature and it could be attributed to the increased electronic conductivity of the carbon film. Hong et al. [16] reported Fe substituted olivine phase, LiMn₁₋ₓFexPO₄ (x = 0, 0.05, 0.1, 0.15. and 0.2) prepared with an appropriate amount of citric acid as the carbon source and subsequently employed planetary ball milling for about 3.5 days before the heat treatment. All the prepared showed similar diffraction patterns, except for a slight shift towards higher angles with increasing concentration of Fe ions and the unit cell shrank continuously as iron was introduced into the system. The cell experienced a discharge capacity of ≈133 and ≈138 mA·h·g⁻¹ at 0.1 C between 2.8 and V by CC mode for 15 and 20% of Fe concentration, and those cells presented solid-solution behavior when the Fe concentration exceeds 10% when compared to the native compound (55 mA·h·g⁻¹ at 0.067 C). Muraliganth and Manthiram [17] reported the solid-solution between LiMnP₀₄ and either LiCoP₀₄ or LiFeP₀₄ by a high energy ball milling procedure with 20% carbon in the final product. The discharge capacity increases significantly from 91 mA·h·g⁻¹ in LiMnP₀₄ to 142 mA·h·g⁻¹ in LiMn₀.₇₅Fe₀.₂₅PO₄, and 155 mA·h·g⁻¹ for LiMn₀.₅Fe₀.₅PO₄ at 0.05 C, whereas LiCoP₀₄ and LiMnP₀₄ solid solution experienced severe capacity fade due to the poor compatibility of the electrolyte.

2.2. Spray Pyrolysis.

Spray pyrolysis is an important method for the preparation of ultrafine powders [18] [19] and it is based on the generation of droplets in a continuous way from a solution containing precursor colloidal particles. Droplets can
be generated by using different techniques, such as ultrasonic transduction [20]. In spray pyrolysis, the generation of droplets is a key step because the droplets act as the nucleation centers and eventually evolve to well-cristallized, dense, and pure particles. Table 2 shows the precursors used in the Spray Pyrolysis method of the resultant LiMnPO4 and composites of this phase. The pyrolysis product is collected in a series of water bubblers at the reactor outlet where the salt product dissolves leaving LiMnPO4. In the recent past, Taniguchi and co-workers [21]-[26] reported the synthesis of LiMnPO4 by spray pyrolysis followed by wet ball milling with 10% acetylene black and ethanol to make the carbon composite. Finally, the composite was fired at 500°C for 4 h in a N2 + 3% H2 environment and found that discharge capacity increases with the charge cut-off voltage. The influence of surface area on the electrochemical performance of LiMnPO4 was also reported by the same authors by adjusting the firing temperature and increasing acetylene black concentration (20%). The solid solution between LiMnPO4 and LiCoPO4 was also reported by the same group using the spray pyrolysis technique [26]. The prepared LiCoMnx−PO4 (x = 0, 0.2, 0.5, 0.8 and 1) powders were milled with 10% wt% acetylene black in ethanol by high energy ball-milling to form composites with carbon. The cells were tested at a 0.5 C rate and delivered an initial discharge capacity of 165 mA·h·g−1 at x = 0, 136 mA·h·g−1 at x = 0.2, 132 mA·h·g−1 at x = 0.5, 125 mA·g·h−1 at x = 0.8 and 132 mA·g·h−1 at x = 1.0, respectively.

Oh et al. [27]-[29] continued the work of ultrasonic spray pyrolysis initiated by Taniguchi and co-workers with spherical size LiMnPO4 particulates. Carbon coating over the particulates was employed by mixing with sucrose, which was followed by ball milling at a speed of 100 rpm for 20 h and subsequently heat treated with different calcination temperatures (550°C, 650°C and 700°C in Ar-H2 atm) ball milling followed by a sintering process led to the destruction of the spherical shape morphology and the final carbon content in the composite was found to be ≈3 wt%. It is obvious that increasing the calcination temperature results in an increase in crystallite size (52, 56 and 60 nm for 550°C, 650°C and 700°C) and decrease in specific surface area.

2.3. Co-Precipitation

This method needs a shorter reaction time and lower temperature compared with the solid state reaction. The particle size can reach the nanometer level and this reduced size can help to enhance the charge-discharge performance especially at big current condition. The inadequacies inhibiting the mass production are the complex process and large power consumption. Table 3 shows the precursors used in the co-precipitation method of the

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Mn Precursor</th>
<th>PO4 Precursor</th>
<th>Metal Dopant</th>
<th>Carbon Source</th>
<th>Product</th>
<th>Discharge Capacity (mA·h/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO3</td>
<td>Mn(NO3)2·6H2O</td>
<td>H3PO4</td>
<td>Acetylene Black</td>
<td>LiMnPO4/C</td>
<td></td>
<td>165</td>
<td>[21]</td>
</tr>
<tr>
<td>LiNO3</td>
<td>Mn(NO3)2·6H2O</td>
<td>H3PO4</td>
<td>Acetylene</td>
<td>LiMnPO4/C</td>
<td></td>
<td>136</td>
<td>[22]</td>
</tr>
<tr>
<td>LiNO3</td>
<td>Mn(NO3)2·6H2O</td>
<td>H3PO4</td>
<td>Acetylene Black</td>
<td>LiMnPO4/C</td>
<td></td>
<td>132</td>
<td>[23]</td>
</tr>
<tr>
<td>LiNO3</td>
<td>Mn(NO3)2·6H2O</td>
<td>H3PO4</td>
<td>Acetylene Black</td>
<td>LiMnPO4</td>
<td></td>
<td>125</td>
<td>[24]</td>
</tr>
<tr>
<td>LiNO3</td>
<td>Mn(NO3)2·6H2O</td>
<td>H3PO4</td>
<td>Carbon Black</td>
<td>LiMnPO4/C</td>
<td></td>
<td>132</td>
<td>[26]</td>
</tr>
<tr>
<td>LiNO3</td>
<td>Mn(NO3)2·6H2O</td>
<td>Fe(NO3)3·9H2O</td>
<td></td>
<td>LiMn0.5Fe0.5PO4</td>
<td>75 - 110</td>
<td>[32]</td>
<td></td>
</tr>
<tr>
<td>LiNO3</td>
<td>Mn(NO3)2·6H2O</td>
<td>Fe(NO3)3·9H2O</td>
<td></td>
<td>LiMn0.85Fe0.15PO4</td>
<td>125 - 140</td>
<td>[33]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Mn Precursor</th>
<th>PO4 Precursor</th>
<th>Metal Dopant</th>
<th>Carbon Source</th>
<th>Product</th>
<th>Discharge Capacity (mA·h/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCO3</td>
<td>MnC2O4·2H2O</td>
<td>NH4H2PO4</td>
<td>Acetylene Black</td>
<td>LiMnPO4/C</td>
<td></td>
<td>[30]</td>
<td></td>
</tr>
<tr>
<td>LiH2PO4</td>
<td>Mn(CH3CO2)2·4H2O</td>
<td>Fe(CH3CO2)3·4H2O</td>
<td>Acetylene Black</td>
<td>LiMn0.85Fe0.15PO4/C</td>
<td>75 - 110</td>
<td>[32]</td>
<td></td>
</tr>
<tr>
<td>LiH2PO4</td>
<td>Mn(CH3CO2)2·4H2O</td>
<td>Fe(CH3CO2)3·4H2O</td>
<td>Acetylene Black</td>
<td>LiMn0.85Fe0.15PO4</td>
<td>125 - 140</td>
<td>[33]</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Precursors used in the spray pyrolysis method of the resultant powders.

Table 3. Precursors used in the co-precipitation method of the resultant powders.
resultant LiMnPO₄ and composites of this phase. Non-stoichiometries proportions of lithium deficient (Li₀.₅MnPO₄ and Li₀.₈MnO₄) and rich phases (Li₁.₁MnPO₄ and Li₁.₂MnPO₄) were synthesized and reported by Xiao et al. [30] using co-precipitation followed by a solid-state approach with ball milling of carbon.

In all the non-stoichiometric compounds of LiₓMnPO₄ phases, traces of impurities like Mn₂P₂O₇ or Li₃PO₄ unavoidably co-existed with the native phase. The observed impurity phases were consistent with the phases observed in another olivine compound such as LiFePO₄ [30] [31]. The half-cells comprising LiMnPO₄, Li₁.₁MnPO₄ and Li₁.₂MnPO₄ phases displayed almost the same initial discharge capacity of ≈124 mA·h·g⁻¹ at 0.05 C rate between 2 and 4.5 V by CC-CV mode, whereas Li₀.₅MnPO₄ and Li₀.₈MnO₄ exhibited ≈75 and 110 mA·h·g⁻¹, respectively. Oh et al. [32] reported the reduction of polarization of the electrode and the least amount of Mn dissolution in C-LiMn₀.₅Fe₀.₅PO₄ by a precipitation technique. Initially, olivine LiMn₀.₅Fe₀.₅PO₄ was carbon coated with carbon (3.3 wt%) and it delivered a discharge capacity of ≈125 and ≈140 mA·h·g⁻¹ at 0.05 C rate at room temperature and 55°C, respectively, between 2.7 and 4.5 V vs Li by CC-CV mode. The same group also reported the performance of micron-sized nanoporous C-LiMn₀.₈₅Fe₀.₁₅PO₄ with high volumetric capacity [33].

### 2.4. Hydrothermal and Solvothermal Routes

Hydrothermal and solvothermal synthesis is a chemical process that occurs in an aqueous solution of mixed precursors above the boiling temperature of water and alcohol respectively. On these routes, it is possible to avoid the calculation step and obtain pure powders directly from the heated solution. However, if the carbon coating is desired, it is necessary to carry out the calcination step at high temperatures. During the synthesis, heated water or alcohol accelerates the diffusion of particles and the crystal growth is relatively fast. Both routes are typically carried out in a closed system called autoclave and there are less environmental concerns than many other powder production technologies.

Therefore, hydrothermal and solvothermal synthesis is a simple, clean and relatively low-cost methods that can be used to produce powders with high uniformity and purity [35]-[37]. Table 4 shows the precursors used in the hydrothermal and solvothermal routes of the resultant LiMnPO₄ and composites of this phase. Fang et al. [38] [39] reported the successful preparation of LiMnPO₄ plates by a simple hydrothermal route in a basic medium at

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Mn Precursor</th>
<th>PO₄ Precursor</th>
<th>Metal Dopant</th>
<th>Carbon Source</th>
<th>Product</th>
<th>Discharge Capacity (mA·h·g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂SO₄</td>
<td>MnSO₄</td>
<td>NH₄H₂PO₄</td>
<td></td>
<td></td>
<td>LiMnPO₄</td>
<td>68</td>
<td>[38] [39]</td>
</tr>
<tr>
<td>LiOH</td>
<td>MnSO₄·H₂O</td>
<td>H₃PO₄</td>
<td>Mg(NO₃)₂·6H₂O</td>
<td>NiSO₄·6H₂O</td>
<td>LiMnₙ₋ₓ(MgNiCu)PO₄</td>
<td>107</td>
<td>[40]</td>
</tr>
<tr>
<td>LiPO₄</td>
<td>MnPO₄</td>
<td>H₃PO₄</td>
<td></td>
<td>Carbon black</td>
<td>LiMnPO₄/C</td>
<td>49 - 107</td>
<td>[41] [42]</td>
</tr>
<tr>
<td>LiH₂PO₄</td>
<td>MnCO₃</td>
<td>FeC₂O₄·2H₂O</td>
<td></td>
<td>Acid lactone</td>
<td>LiMn₁₋ₓFeₓPO₄/C</td>
<td>50 - 65</td>
<td>[43]</td>
</tr>
<tr>
<td>LiOH</td>
<td>Mn(CH₃COO)₂·4H₂O</td>
<td>H₃PO₄</td>
<td></td>
<td>Multiwalled Carbon nanotubes (MWCNT)</td>
<td>LiMnPO₄/MWCNT</td>
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<tr>
<td>LiOH</td>
<td>MnSO₄·H₂O</td>
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<td></td>
<td></td>
<td>LiMnPO₄</td>
<td>67</td>
<td>[47]</td>
</tr>
<tr>
<td>LiOH</td>
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<td>H₃PO₄</td>
<td>CuSO₄·5H₂O</td>
<td>LiMnₙ₋ₓCuₓPO₄</td>
<td>LiMn₀.₈₅Fe₀.₁₅PO₄</td>
<td>76 - 101 - 121</td>
<td>[48]</td>
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<tr>
<td>LiOH·H₂O</td>
<td>MnSO₄·H₂O</td>
<td>H₃PO₄</td>
<td></td>
<td></td>
<td>LiMnPO₄</td>
<td>92 - 120 - 126 - 147</td>
<td>[49]</td>
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<tr>
<td>Li₂PO₄</td>
<td>MnSO₄·5H₂O</td>
<td></td>
<td></td>
<td></td>
<td>LiMnPO₄</td>
<td>135</td>
<td>[50]</td>
</tr>
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</table>
200°C. The results clearly indicate that the prepared materials were in the nanometric range and actively participated in the electrochemical reaction in which plate-like LiMnPO$_4$ ball milled with 20% of carbon delivered a discharge capacity of 68 mA·h·g$^{-1}$ between 3 and 4.5 V at 1.5 mA·g$^{-1}$. Divalent cation doping (10%) such as Mg, Ni, Co, Zn, and Cu, was reported by Chen et al. [40] via a hydrothermal approach. The substitution of Mn sites leads to a decrease in lattice parameter values. The cell volume also decreased 0.8% for Mg$_{2+}$, 0.6% for Ni$_{2+}$, 0.3% for Cu$_{2+}$, and 0.4% for Zn$_{2+}$ substitution consistent with their smaller ionic radii. A citric acid assisted facile one step solvothermal (equiv. volume mixture of water and ethanol) procedure was adopted by Wang et al. [41]-[42] to synthesize the microspherical LiMnPO$_4$ at 300°C.

The obtained microspherical particles were mixed with glucose followed by heat treatment for carbon coating. The Li/LiMnPO$_4$ cell displayed a discharge capacity of 107 mA·h·g$^{-1}$ at 0.01 C with an appreciable plateau around ≤4.2 V vs Li. As expected, increasing the current rate leads to poor cell performance; for example, at 1 C test cell presented a discharge capacity of 49 mA·h·g$^{-1}$. By introducing cetyltrimethylammonium bromide (CTAB) as a chelating agent in the above solvent mixture at relatively low temperature conditions (240°C) LiMnPO$_4$ nanorods can be obtained. The storage performance of nanoplatelets of LiMnPO$_4$ and LiFe$_{0.5}$Mn$_{0.5}$PO$_4$ was studied by Saravanan et al. [43] using a simple solvothermal method at 250°C for 8 h with gluconic acid p-lactone. The final LiMnPO$_4$ and Fe doped phases comprised of 10 wt% carbon. The test cells exhibited a discharge capacity of ≈50 and 65 mA·h·g$^{-1}$ between 2.3 and 4.5 V by CC mode. Further, the same group of authors continued the work on solid-solutions of LiMn$_{1-x}$Fe$_x$PO$_4$ nanotubes by tuning various parameters, such as source materials, precursor concentration, effect of solvent, synthesis temperature and conducting coatings using the same approach. Manthiram and co-workers [44]-[46] reported a facile route to produce nanostructured LiMnPO$_4$ by a microwave assisted hydrothermal or solvothermal approach. In the hydrothermal approach, glucose is used as the source material for carbon, whereas MWCNTs were painted on the surface to enable a conducting network for LiMnPO$_4$ nanorods by the solvothermal route. LiMnPO$_4$ prepared by the above mentioned rousted displayed a monotonous charge-discharge curve and exhibited a discharge capacity of ≈15 to 45 mA·h·g$^{-1}$.

Ji et al. [47] also followed a similar approach to yield LiMnPO$_4$ nanostructures using citric acid and sodium decyl benzene sulfonate (SDBS) as an additive to tune the morphology of the final product. Also reported the kinetic behavior during Mg$_{2+}$ substitution on Mn site compounds were prepared by a hydrothermal reaction and consequently ball milled carbon (20 wt%) before making electrodes. Increasing the concentration of Mg$_{2+}$ (LiMn$_{1-x}$Mg$_x$PO$_4$, x = 0 ≤ 5) provides substantial improvement in the thermal stability of the phase. Ni and Gao [48] reported the synthesis of Cu$_{2+}$ substituted LiMnPO$_4$ by an ascorbic acid mediated synthesis. The obtained particles (=100 nm) were carbon coated by carbonization of sucrose at 600°C and carbon content of 2.4 wt% was obtained in the final product. In the range of 2.2 - 4.5 V (CC-CV mode), test cells delivered a reversible capacity of 101, 121 and 76 mA·h·g$^{-1}$ for LiMnPO$_4$, LiMn$_{0.98}$Cu$_{0.02}$PO$_4$ and LiMn$_{0.95}$Cu$_{0.05}$PO$_4$ phases, respectively. Wang et al. [49] reported the solvothermal synthesis of LiMnPO$_4$ nanoplates and rods using sodium dodecyl benzene sulfonate (SDBS). The synthesized powders were carbon coated through chemical vapor deposition (CVD) using methylbenzene as the carbon source and argon as the carrier gas. The authors compared the carbon coating technique with the conventional high energy ball milling (BM) procedure.

The discharge capacities of plate-CVD, Rod-CVD, Plate-BM and Rod-BM were 147, 126, 120 and 92 mA·h·g$^{-1}$, respectively, between 2.5 and 4.9 V at 0.05C at room temperature by CC mode. Recently, Dokko et al. [50] suggested the synthesis of LiMnPO$_4$ nanoparticles by reacting Li$_3$PO$_4$ (solid) with molten aqua-complexes of MnSO$_4$ under hydrothermal conditions at 190°C. Later, the obtained LiMnPO$_4$ particles were carbon coated using sucrose with subsequent heat treatment at 700°C. The molar ratio of Mn$_6$ and H$_2$O in the reactor was varied by adding water to the reaction mixture. When x = 7.8, 50 nm size LiMnPO$_4$ particles were obtained which delivered a discharge capacity of ≈135 mA·h·g$^{-1}$ at 0.1 C between 2 and 4.5 V by CC-CV mode.

2.5. Sol-Gel Synthesis

Sol-gel synthesis is a low temperature, wet chemical approach, which is often used for the preparation of metal oxides or other specific compositions. Standard sol-gel synthesis involves the formation of a sol, *i.e.* a stable colloidal suspension of solid particles in a solvent, and the gelation of the sol to form a gel consisting of interconnected rigid skeleton with pores made of colloidal particles. The properties of the gel are determined by the particle size and cross-linking ratio. The gel can then be dried to form xerogel, which shows reduced volume [51]-[54].

To obtain the final powder products, all liquids need to be removed from the surfaces of pores by a heat
treatment carried out at elevated temperatures, which also reduces the number and connectivity of pores, known as densification [53] [54]. Reaction parameters such as temperature, time, pH, precursor, solvent, concentration and viscosity, etc., are of importance for the formation and ultimate morphology (particle size and shape, pore size, and porosity) of the obtained powders. In sol-gel synthesis, the surfaces of the powder products are controlled from the beginning of the reactions. In addition, sol-gel synthesis is low cost and does not require high processing temperature, and powders produced by this method have the advantages or precise stoichiometry control, high purity, uniform structure and very small size. Table 5 shows the precursors used in the sol-gel method of the resultant LiMnPO₄ and composites of this phase. Ethylene glycol assisted synthesis of LiMnPO₄ (M = Fe, Mn and Co) nanostructures was reported by Yang and Xu [55] to enable in situ carbon coating. In situ carbon coating over LiMnPO₄ particles by using organic precursors was successful and it was found that 3.3 wt% of carbon was covered on the surface after the phase formation at 700°C in a N₂ atmosphere. The Li/LiMnPO₄ cell was cycled between 2.5 and 4.5 V in CC mode and delivered a reversible capacity of 85 and 42 mA·h·g⁻¹ at 0.01 and 0.05 C rates, respectively. Kwon et al. [56] successfully synthesized nanosized (140 - 130 nm) LiMnPO₄ particles by a glycolic acid assisted sol-gel approach. The prepared LiMnPO₄ was ball milled with 20 wt% carbon size reduction as well as to enable carbon coating. The cycling profiles indicate reduction of particle size from 830 to 140 nm which resulted in improved electrochemical performance (~134 mA·h·g⁻¹ for 140 nm particles) between 2.3 and 4.5 V at 0.1 C. At 1 C, 140 nm particles exhibited a reversible capacity of ≈81 mA·h·g⁻¹, whereas 270 nm particles showed a reversible capacity of ≈5 mA·h·g⁻¹. A liquid phase synthesis was also reported by Doi et al. [57] to reduce the particle size in the presence of long chain oleic acids comprising 18 atoms of carbon. For this synthesis, the total reaction was completed at less than 300°C resulting in the formation of LiMnPO₄. The obtained compound delivered a discharge capacity of 6 mA·h·g⁻¹ between 3 and 4.5 V at 0.01C by CC mode. After heat treatment at 500°C for 1 h in Ar, the long chain oleic acid was burned and converted to carbon. Isovalent and aliovalent doping (Mg²⁺, Fe²⁺, Co²⁺, V³⁺ and Gd³⁺) on Mn²⁺ sites reported by Yang et al. [58] and such phases were prepared by solution phase reaction using citric acid as the carbon source. The precursors were ball-milled for 10 h in a planetary ball miller and fired at 700°C for 20 h in a N₂ atmosphere. The substitution in Mn sites (LiMn₀.95M₀.05PO₄, M = Mg, V, Fe, Co and Gd) clearly revealed the increase in unit cell volume for all cases, except for Fe²⁺. The cell delivered a discharge capacity of 45, 61, 32, 102 and 59 mA·h·g⁻¹ at room temperature (25°C), and 113, 120, 95, 149, and 117 mA·h·g⁻¹ at an elevated temperature (50°C) for Mg, V, Fe, Co, and Gd substitutions, respectively, between 2.7 and 4.4 V in CC-CV mode. Preparation of LiMnPO₄ composites was suggested by Herrera et al. [59]. The authors intended to increase the surface area, thereby achieving full performance of the material by utilizing a conventional coating technique. It is worth mentioning that addition of glucose. This indicates that the presence of carbon coating during the formation of crystallites increases the number of nucleation sited and

<table>
<thead>
<tr>
<th>Li Precursor</th>
<th>Mn Precursor</th>
<th>PO₄ Precursor</th>
<th>Metal Dopant</th>
<th>Carbon Source</th>
<th>Product</th>
<th>Discharge Capacity (mA·h·g⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(COOCH₃)·2H₂O</td>
<td>Mn(CH₃COO)·2H₂O</td>
<td>H₂PO₄</td>
<td>LiMnPO₄</td>
<td>42 - 85</td>
<td>[55]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>Mn(CH₃COO)·2H₂O</td>
<td>H₂PO₄</td>
<td>LiMnPO₄</td>
<td>5 - 81 - 134</td>
<td>[56]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(COOCH₃)·2H₂O</td>
<td>MnSO₄·H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Mg(NO₃)₂</td>
<td>LiMnPO₄</td>
<td>[57]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li(COOCH₃)·2H₂O</td>
<td>Mn(CH₃COO)·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Co(CH₃COO)₂</td>
<td>LiMn₀.95M₀.05PO₄, M = Mg, V, Fe, Co, and Gd respectively</td>
<td>45, 61, 32, 102 and 59 at 25°C and 113, 120, 95, 149, and 117 at 50°C</td>
<td>[58]</td>
<td></td>
</tr>
<tr>
<td>LiOH</td>
<td>Mn(CH₃COO)·2H₂O</td>
<td>H₂PO₄</td>
<td>Glucose</td>
<td>LiMnPO₄/C</td>
<td>[59]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiNO₃</td>
<td>Mn(NO₃)₂</td>
<td>H₂PO₄</td>
<td>SWNT</td>
<td>LiMnPO₄/SWCN</td>
<td>70</td>
<td>[58]</td>
<td></td>
</tr>
<tr>
<td>Li(COOCH₃)·2H₂O</td>
<td>Mn(CH₃COO)·2H₂O</td>
<td>NH₄H₂PO₄</td>
<td>SWNT</td>
<td>LiMnPO₄/SWCN</td>
<td>140</td>
<td>[58]</td>
<td></td>
</tr>
<tr>
<td>Li(COOCH₃)·2H₂O</td>
<td>MnSO₄·H₂O</td>
<td>NH₄H₂PO₄</td>
<td>Co(CH₃COO)₂</td>
<td>LiMn₀.91Co₀.09PO₄</td>
<td>148</td>
<td>[58]</td>
<td></td>
</tr>
</tbody>
</table>
leads to increases in the size of the particle. Nithya et al. [60] reported synthesis of LiMn_{0.9}Co_{0.09}PO_4 by a glycine assisted sol-gel approach with the particle size ranging from 50 to 300 nm. The resultant phase was ball milled with the desired amount of carbon (acetylene black 30 wt%) to yield a high performance cathode. Li-Co_{0.09}Mn_{0.91}PO_4/C delivered a maximum discharge capacity of 162 mAh g^{-1} between 3 and 4.9 V vs Li (CC mode) at 0.1 C when compared to 70, 140 and 148 mAh g^{-1} for LiMnPO_4, LiMnPO_4 and LiCo_{0.09}Mn_{0.91}PO_4 respectively.

As a final remark, it can be observed that the highest Discharge Capacity is reported for LiMnPO_4/C (165 mAh/g, Table 2) synthesized by spray pyrolysis, the same composite synthesized by hydrothermal or solvothermal (147 mAh/g, Table 4) and by solid state reaction (144 mAh/g, Table 1). High values are also reported for LiMn_{0.8}Fe_{0.2}PO_4 (155 mAh/g, Table 1) by solid state reaction, LiMn_{0.8}Fe_{0.2}PO_4 (140 mAh/g, Table 3) by chemical co-precipitation, and LiMn_{0.95}Fe_{0.05}PO_4, (M = Co) (149 mAh/g, Table 5) by sol-gel method.

These results suggest that those synthesis methods that allow a better control of particle size and morphology can offer a better potential to improve the Discharge Capacity. Another path can be combined Mn with Fe and Co. It also can be observed that the highest Discharge Capacity can be reached for the LiMnPO_4/C, and then the addition of Carbon source is also a topic that deserves attentions.

Other phosphates compounds can be used as cathodes in lithium ion batteries. LiCoPO_4 (100 mA h g^{-1}) [61] [62] has higher open circuit voltages, but lower dielectric capacity than those of LiMnPO_4. In addition, Co_2P_4 has been observed to be formed in delithiated LiCoPO_4 electrode, which degrades the lifetime and can be a safety concern as oxygen is involved during the decomposition reaction. Mixtures of phosphates, including Li-CoPO_4 or LiFePO_4 (170 mA h g^{-1}) [63], with LiMnPO_4, have been used for cathode materials. In such mixtures, the operating voltage increases with increasing manganese content [64] [65], while capacity increases with increasing iron content [1]. Although LiNiPO_4 also forms the olivine structure [1] it is no typically used as a cathode material. However, nickel has been added to other phosphate cathode materials. Not considering Olivine Phosphate, few examples can be mentioned that can be considered potentially useful: LiCoO_2 (140 mA h g^{-1}), Li,Mn_{0.5}O_4 (125 mA h g^{-1}) and nanostructured Vanadium Oxide (VO_x) with Lithium intercalation capacities [66]. It must be mentioned that VO_x can go through structural breakdown during redox cycles. In this scenery, LiMnPO_4 can be considered as a promising material for battery cathode.

3. Conclusions

LiMnPO_4 have been reviewed focusing mainly on the synthesis method and how to improve the electrochemical properties performance for batteries cathode. For LiMnPO_4 small particle size well-shaped crystals are important for enhancing the properties. In particles with a small diameter, the Li ions may diffuse over shorter distances between the surfaces and center during Li intercalation and de-intercalation contributing to the charge/discharge reaction. The variety of synthesis methods offers more possibilities to control desirable structures and high electrochemical performance. However, it is often challenging to obtain all the desired properties.

Typically, solid state methods are of importance in terms of obtaining ordered crystal structure, but they require higher treatment temperature and longer process time, which may lead to larger particle size and lower electrochemical capacity. On the other hand, sol-gel method gives high purity, small particle size, uniform size distribution, and hence relatively higher electrochemical capacity, but additional solvent cost and environment issues are major disadvantages of these methods. Many solid-state and solution-based methods are good candidates for the mass production of LiMnPO_4 powders at industrial scale; however the cost, productivity, reproducibility and complexity of these methods must be taken into consideration.

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References


