Enhanced electrochemical performance of <30 nm thin LiMnPO₄ nanorods with a reduced amount of carbon as a cathode for lithium ion batteries

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5–10 nm thin rod shaped LiMnPO₄ nanoparticles are synthesized by an improved thermal decomposition method. The synthesis parameters such as the concentration of surfactants, reaction temperature and time, as well as the presence of a solvent play a critical role in the formation of spherical, thin or thick nanorods, and needle-shaped particles of LiMnPO₄. A washing procedure to efficiently eliminate the surfactants attached to the surface of LiMnPO₄ nanoparticles is presented, avoiding thermal treatment at high temperatures. A nanocomposite LiMnPO₄ electrode provides a discharge capacity of 165 mAh/g at 1/40 C and 66 mAh/g at 1 C with only 10 wt% of total carbon additive. The characteristics of as-synthesized and low amount of carbon coated LiMnPO₄ are described as well as their electrochemical properties.

1. Introduction

Commercial lithium ion batteries are cobalt-based and limited to applications in small portable electronic devices due to the practical capacity limitation [1–3], cost and safety issues [4,5]. Future energy storage devices need advanced materials to fulfill the higher demands in terms of energy density and safety, while reducing the cost and environmental concerns. Olivine LiMPO₄ (M = Fe, Mn, Co and Ni) materials recently gained interest as alternative cathode material because of their thermal/chemical stability and low cost [6]. Contrary to metal oxide materials such as LiCoO₂, LiMn₂O₄, LiNiO₂, LiMnO₂, etc., olivines have PO₄³⁻ polyions, which make the structure stable vs. lithium insertion/extraction [6,7]. Among the olivine materials, LiFePO₄ was firstly developed and is available on the market. However, its energy density related with the low cell voltage (3.4 V vs. Li) and the theoretical capacity (170 mAh/g) limits its use in electric vehicles [7]. LiMnPO₄ has also 170 mAh/g of theoretical capacity but has a higher cell voltage of 4.1 V vs. Li, thus providing a higher energy density than LiFePO₄ [8,9]. In order to allow the Mn³⁺/²⁺ redox reaction in a LiMnPO₄ cathode, the material needs to be both ionically and electronically conductive for Li⁺ diffusion and electron transport, respectively. However, pure LiMnPO₄ material suffers from poor intrinsic electronic conductivity [10,11]. To improve the electrochemical kinetics, several groups, including previous work by us, reported the enhanced electrochemical properties, combining both, reduced particle size of LiMnPO₄ and carbon coating [12–15]. Nanosized LiMnPO₄ provides the shorter lithium ion diffusion path within a single particle compared to micromized LiMnPO₄ [16]. Most highly performing LiMnPO₄ materials were achieved by adding a large amount of carbon (15–30 wt%) in order to increase the electronic conductivity [12–15,17–20].

Nano-LiMnPO₄ has been prepared by various wet chemical methods such as hydrothermal [21–23], thermal decomposition [20,24], solvothermal [17,25], polyol methods [15], etc. Wet chemical methods are preferable as they allow perfect mixing of precursors, better homogeneity and more regular morphology to obtain nanosized particles. However, a drawback of this method is the complete removal of organic residuals, which prohibit the conductivity of the so synthesized material. Doi et al. obtained LiMnPO₄ having uniform particle sizes of 7 nm via the thermal decomposition method. Its initial discharge capacity was only about 6 mAh/g even though the charge and discharge rates were extremely slow (1/100 C) [24]. The poor electrochemical performance of LiMnPO₄ even with 7 nm sized particles is explained by the presence of remaining oleic acid on LiMnPO₄ particles after the synthesis, preventing Li⁺ and electron transfer. While the thermal treatment allows to burn out the attached oleic acid on LiMnPO₄, this process results in 40–125 nm thick rod shaped LiMnPO₄ instead of 7 nm spherical shape of particles, providing 65 mAh/g of capacity at 1/100 C with an additive of 25 wt% of carbon. Thus, to make ultrafine nano-LiMnPO₄ particles electrochemically active, the clean surface of nano-LiMnPO₄ particles without thermal treatment is necessary.

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The carbon coating must be permeable for Li$^+$ ions in the electrolyte to be penetrated into the active material. Nanostructured composites consisting of the cathode material and a conductive additive allow to utilize theoretical capacity [13,14,26]. There are several parameters to be taken into account in order to make a nanocomposite applicable as a cathode material for lithium ion batteries. Increasing the amount of carbon in the electrode enhances its electronic conductivity [12], but as carbon is not electrochemically active, minimizing the amount of carbon is desired for increasing the loading of active material within a given volume of lithium ion batteries in order to increase the energy density. This is particularly important for large applications such as electric vehicles where high power and energy density are required. In addition, the nanostructure of the composite can be dependent on the morphology and surface area of the carbon additive as well as its preparation method. For example, porous carbon black is spherical and has high surface area, [27–29] while graphite is a sheet structure and has relatively low surface area [28]. Thus, nanocomposites of LiMnPO$_4$ with 20% or more high surface area carbon black were shown to provide large contact area with the active material, leading to homogeneous nanostructured composites [13,15].

So far, the production of electrochemically active and surfactant-free nanoparticulate LiMnPO$_4$ <30 nm remains a challenge, together with the reduction of carbon amount while...
maintaining high performance of nanocomposite C-LiMnPO₄ electrode. In this study, we address the questions how to reduce efficiently the LiMnPO₄ particle size and the influence of the reaction conditions on the shape of the nanoparticles, how to eliminate organic residues on the surface of the latter, and how to reduce the amount of added carbon for the production of the electrode, while still maintaining excellent electrochemical properties.

2. Experimental

LiMnPO₄ material is prepared by the thermal decomposition method [24] without or with high boiling temperature solvent of benzyl ether. 3 mmol Mn(NO₃)₂·6H₂O and 3 mmol LiOH·H₂O are dissolved in 9 or 27 mmol oleic acid at 120 °C. In case of using a solvent, 20 ml of benzyl ether was then added to the solution. When the temperature of the solution reaches 230 °C, 9 or 27 mmol oleylamine and 3 mmol H₂PO₄ are injected. The solution is kept stirring vigorously and is held at 230 °C for 1.5 h. Then the temperature is increased to between 265 and 280 °C for 1–4 h. After the reaction, the suspension was centrifuged to collect the sedimented black powder. This material is rinsed with ethanol and hexane and centrifuged.

In order to remove the organic residue after rinsing, the collected black material was dispersed in 15 ml chloroform in a glass tube. Deionized water containing 0.1 g of citric acid is added to the tube, forming a two-phase system. The black chloroform solution clearly separates from the water phase in the tube. The mixture is stirred while heating overnight at 85 °C. The transparent water became a gray suspension after ligand exchange. This gray suspension was centrifuged to collect the gray powder.

As-synthesized LiMnPO₄ after ligand exchange was mixed with 5 or 7 wt% of carbon black using a ball mill (RETSH) for 10–90 min. As-synthesized LiMnPO₄ material and C-LiMnPO₄ composite have been characterized by various methods. X-ray diffraction using Mo-radiation (give machines here and below) was employed to identify the phase. Brunauer–Emmett–Teller (BET) nitrogen adsorption method was applied to measure the specific surface area. Thermogravimetric analysis (TGA) was used for thermal analysis. The morphology and the size of particles were determined by scanning electron microscopy (SEM, Philips XL30), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). Fourier transform infrared (FT-IR) was employed for the surface analysis. The crystallite size is calculated by the Scherrer equation \((d = 0.9\lambda/(B \cos \theta))\), where \(d\) is the mean crystallite size in volume-weight, \(\lambda\) is the wavelength of the X-rays, \(B\) is the width of a peak at a half maximum due to size effects assuming that there is no strain, \(K\) is a constant value of 0.89, and \(\theta\) is the Bragg angle).

For the electrochemical property, the electrode was prepared on aluminium foil with C-LiMnPO₄ composite, carbon black and polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The weight ratio of active material LiMnPO₄, carbon black and the binder was 80:10:10. After drying the electrode at 120 °C under vacuum overnight, the working electrode was assembled with lithium metal as counter electrode, ethyl carbonate (EC) and dimethyl carbonate (DMC) mixture in 1:1 volume ratio with 1 M LiPF₆ electrolyte and a separator from Celgard in Swagelok cell. Potentiostat and Galvanostat technique were applied to obtain the electrochemical property of C-LiMnPO₄ composite electrodes using Arbin 2000 instrument.

3. Results and discussion

3.1. Synthesis of LiMnPO₄ nanoparticles

In a first step we tried to reproduce the spherical LiMnPO₄ particles of 7 nm obtained by Doi et al., repeating their synthetic procedure [24]. However, under the described conditions, we could not reproduce their results, obtaining nanorods of 5 nm with very low yield (<30%) shown in Fig. 1(a) (hereafter referring to as phase N for needle). In order to improve the yield, we used benzyl ether as solvent because it has a high boiling point and is a good solvent for all used precursors \((\text{LiOH·H}_2\text{O}, \text{Mn(NO}_3\text{)}_2·6\text{H}_2\text{O}, \text{and H}_2\text{PO}_4\)) during the synthesis. The yield of LiMnPO₄, identified by XRPD, could be improved to over 78%. In the following, we investigated the shape and size of LiMnPO₄ nanoparticles obtained as a function of reaction temperature, reaction time and the relative amounts of the surfactants.

The influence of the concentration of surfactant and reaction time on the thickness on size and shape of LiMnPO₄ is shown in Fig. 1(b)–(d). A molar ratio of 9:1 of oleic acid and precursor with the reaction temperature of 265 °C for 1 h provides spherical, slightly elongated shapes of particles of 30–50 nm shown Fig. 1(b) (hereafter referring to as phase S for spherical). After 4 h of reaction time and otherwise same conditions, we obtained rod-shaped LiMnPO₄ of 30 nm × 100 nm (Fig. 1(c)). Lowering the concentration of the surfactant to a molar ratio 3:1 of oleic acid to precursors, we obtain rod-shaped particles, which are thinner (10–20 nm) than the ones obtained before (Fig. 1(d) hereafter referring to as phase NR for nanorods).

The temperature during the synthesis also influences the thickness of nanorod shapes, as shown in Fig. 1(d)–(f). For a reaction time of 1.5 h, a high temperature of 280 °C gives 50 nm thick nanorods
(Fig. 1(e)) compared to 10 nm at 265 °C (Fig. 1(d)). Reducing the reaction time to 1 h at 280 °C leads to shorter rodlike particles with (15–50) nm × (62–165) nm (Fig. 1(f)) (hereafter referring to as phase TR for thick nanorods).

For the synthesis aspects, we can conclude that the smallest particles are still obtained without solvent but with very low yield, while we obtain excellent yields of as small as 10 nm sized LiMnPO₄ particles in presence of a solvent. The external parameters like the concentration of surfactant, the reaction temperature and the duration of the synthesis play an important role to control the shape and size of nanoparticles. The best conditions in our studies are the ratio of 3:1 of oleic acid to precursors, the reaction temperature 265 °C and the time of 1.5 h, leading to 10 nm × 30 nm of LiMnPO₄ particles.

<table>
<thead>
<tr>
<th>Shape of particles</th>
<th>Size of crystallite (nm)</th>
<th>S_{BET} (m²/g)</th>
<th>Particle size by S_{BET} × (nm)</th>
<th>Size by TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Needle and rod</td>
<td>16</td>
<td>80.35</td>
<td>22</td>
<td>5 × (30–100)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(30–50) × (200–300)</td>
</tr>
<tr>
<td>Thin rod</td>
<td>18</td>
<td>98.78</td>
<td>18</td>
<td>10–20 × (30–100)</td>
</tr>
<tr>
<td>Sphere</td>
<td>21</td>
<td>35.07</td>
<td>49</td>
<td>30–50</td>
</tr>
<tr>
<td>Thick rod</td>
<td>24</td>
<td>18.24</td>
<td>95</td>
<td>(15–50) × (62–165)</td>
</tr>
</tbody>
</table>

* The particle size, d, is calculated by the equation of \( d = K/\rho \times S_{BET}^{1/3} \), where \( K \) is the shape factor, \( \rho \) is the density of the material and \( S_{BET} \) is the specific surface area of the material.

The crude material obtained from all these syntheses was found to have organic material on the surface, which we were able to remove with special washing procedure described in Section 3.3. Fig. 1 refers to the particles obtained after the washing process.

3.2. Crystallite size and specific surface area of LiMnPO₄

We determined the crystallite size using Scherrer equation applied to X-ray powder diffractograms (Fig. 2(a)) of our LiMnPO₄ nanoparticles obtained under the different conditions. We chose the XRD peak at 2θ = 11.6º as it has high enough intensity and no shoulder from neighbouring peaks. From the different peak widths of three samples corresponding to phase N, NR and TR in Fig. 1(a),

![Diagram of LiMnPO₄ synthesis](http://doc.rero.ch)

*Fig. 3.* (a) Before ligand exchange; (b) after ligand exchange; (c) a scheme of the process of LiMnPO₄ surface modification; (d) the dark brown LiMnPO₄ material coated with oleic acid and oleylamine (on the left) and light gray one without oleic acid (on the right). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)
(d) and (f), respectively, we can conclude that the crystallite sizes vary between 16 and 24 nm on average. The specific surface areas (SSA) of various shaped and sized LiMnPO₄ are analyzed using N₂ adsorption method. The characteristics of various as-synthesized LiMnPO₄ nanoparticles are summarized in Table 1. The thin nanorod shaped LiMnPO₄ corresponding to Fig. 1(d) obtained the highest SSA of ca.100 m²/g corresponding to 18 nm of particle size assuming spherical particle. The needle shaped nanoparticles have slightly lower SSA, 80 m²/g, due to the small amount of large rod shaped LiMnPO₄ particles observed in Fig. 1(a). The sphere and thin rod shaped LiMnPO₄ particles corresponding to phase S and phase NR, have specific surface areas of ~35 and 99 m²/g, respectively. The characteristics of four samples, phase N, NR, S and TR are summarized in Table 1.

3.3. Washing procedure of LiMnPO₄ nanoparticles

After the synthesis of LiMnPO₄ nanoparticles, the material is described to be rinsed with ethanol and hexane in order to remove the surfactants attached on the surface of LiMnPO₄ [24]. However, the surfactants were not completely eliminated, as indicated by the dark brown color of the product. We observed that for the synthesis in which we use the solvent, the surfactant can be removed better compared to syntheses without solvent – but not totally. As we do not want risk the increase of the particle size by thermal treatment for the removal of organic residues, we tested another “washing” method called “ligand exchange” [30–32]. For this ligand exchange, we start by collecting the material first by using centrifugation after the synthesis. It is then dispersed in CHCl₃. A solution of citric acid in water is added, yielding a two-phase system. (Fig. 3(a)) Mild heating at 80 °C leads to the formation of boiling CHCl₃, forming droplets, which move up through aqueous solution before evaporating. These small droplets are in close contact with the aqueous phase, and the exchange of oleic acid and oleylamine vs. citric acid can occur at the surface of LiMnPO₄ nanoparticles in suspension in these droplets. Citrate decorated LiMnPO₄ nanoparticles are preferably suspended in water rather than CHCl₃, and therefore we observe the phase transfer of the nanoparticles from the organic into the aqueous phase (Fig. 3(b)). The rinsing process is shown in Fig. 3(c). The ligand exchange is accompanied by a color change from dark brown to light gray (Fig. 3(d)). The gray material is confirmed to be LiMnPO₄ by XRPD after ligand exchange and centrifugation (see Supplementary data Fig. S1).

The ligand exchange process on the surface of LiMnPO₄ nanoparticles can be followed by FT-IR shown in Fig. 4. It shows a large difference in the bands at 2900 and 1700/cm responsible for oleic acid and oleylamine [20] marked in green on the black for unwashed sample (i). The sample washed with ethanol/hexane (ii) (in blue) still shows presence of organic ligands, while the red spectrum obtained for LiMnPO₄ after ligand exchange (iii) shows no more such band. It confirms that oleic acid and oleylamine are successfully removed by the ligand exchange method on the surface of LiMnPO₄ nanoparticles.

These finding are confirmed by thermogravimetric analysis (TGA) for the same three samples (see Supplementary data Fig. S2). Unwashed material (i) loses about 15 wt% of the total weight, indicating the amount of remaining surfactants of nanoparticles of LiMnPO₄. 10 wt% of the total weight is still lost after washing with ethanol/hexane (ii), indicating that only 1/3 of surfactant can be removed with this method. In contrast, our ligand exchange method leads to only 2 wt% weight loss (iii), proving the efficacy to remove the organic residues after the synthesis. Another strong advantage of this ligand exchange method is to avoid undesired particle growth compared to heating treatments at high temperatures (>500 °C) as used by Doi et al. [24] upon which the nanoparticles aggregate.

3.4. Nanocomposite of C-LiMnPO₄

In order to make LiMnPO₄ electronically more conductive, carbon black can be added to improve its properties. We have shown previously that addition of carbon black improves the electrochemical properties [13,15]. The typical amount of carbon described in the literature is between 20 and 30 wt% [12,13,15,20].

Among the parameters mentioned in the introduction, we here focus on the lowering of the carbon quantity used to prepare the composite. We chose high surface area of carbon black and the ball milling method to obtain a C-LiMnPO₄ nanocomposite with intimate contact between carbon and LiMnPO₄. Two nanocomposites are prepared by ball milling, with 5 and 7 wt% of carbon having 1000 m²/g of specific surface area, respectively, and the LiMnPO₄ nanoparticles as obtained in Fig. 1(d), thus with the highest surface area of our prepared nanoparticles (referred to as 5C-LiMnPO₄ and 7C-LiMnPO₄, respectively). 7C- and 5C-LiMnPO₄ nanocomposites are investigated by TEM as shown in Fig. 5(a) and (b), respectively. Carbon is dark gray and LiMnPO₄ particles are black in these images. In 7C-LiMnPO₄, the carbon seems better distributed and the LiMnPO₄ active particles are more homogeneously coated compared to 5C-LiMnPO₄, which has more often bare LiMnPO₄ particles without carbon coating on the surface (Fig. 5(b)). We also observed that the shape of the LiMnPO₄ particles is now polyhedral, which is different from the initial rod shape of pristine LiMnPO₄. 7C-LiMnPO₄ nanocomposite is also investigated by SEM (Fig. 5(c) and (d)). It shows a rough surface and agglomerated large, dense particles. EDX confirmed that these agglomerated dense particles consist of C, Mn, P and O elements indicating carbon and LiMnPO₄ material (Supplementary data Fig. S3).

From the microscopic methods, we concluded that the best nanocomposite is obtained with 7 wt% of carbon by ball milling.

3.5. Electrochemical properties

A typical process of making an electrode includes the use of the C-LiMnPO₄, extra carbon and a binder in N-methyl-2-pyrrolidone (NMP). We prepared the electrodes with the nanostructured composite of 7C-LiMnPO₄, additional 3 wt% of carbon black and polyvinylidene fluoride (PVDF) as a binder in order to obtain a 10 wt% of carbon in total. The cathode electrode is assembled in a Swagelok type of cell with lithium metal ribbon as a counter electrode and the commercially available lithium ion battery electrolyte.
In Table 2, the literature results for composite C-LiMnPO₄ material are resumed for their particle size, amount of carbon added (total amount) and the observed capacity. Compared to these results, Fig. 6 shows that our electrode provided 165 mAh/g of discharge capacity, which is 97% of the theoretical capacity, a value so far unprecedented and obtained at a reasonable C-rate. In the literature, high electrochemical performances of LiMnPO₄ electrodes, but lower than ours, are reached only upon adding more than 20 wt% carbon (Table 2). However, we improved the electrochemical property by further reducing the particle size below 50 nm of LiMnPO₄ using only 10 wt% of carbon in total. This result provides that 10 nm of LiMnPO₄ particles can be fully charged and discharged reversibly even with a low quantity of carbon at a reasonable C-rate. This excellent result might be due to the removal of organic material at the surface of the nanoparticles of LiMnPO₄.

We also investigated higher C-rates shown in Fig. 7. The discharge capacities of LiMnPO₄ electrode are 110 and 66 mAh/g at 1/6 C and 1 C. These capacities of 10 wt% of carbon containing LiMnPO₄ nanomaterial are comparable to the ones with ~20 wt% of carbon from other references. The large gap between the charge and the discharge curve at 1 C indicates the resistance of electrode. We currently are optimizing the electrode parameters to reduce its resistance and enhance the performance at high C rates.

Table 2
The comparison of the capacities of LiMnPO₄ electrode with various amount of carbon and LiMnPO₄ particle size.

<table>
<thead>
<tr>
<th>Synthesis methods</th>
<th>Particle size (method)</th>
<th>Total C - amount (wt%)</th>
<th>Carbon source</th>
<th>Capacity (mAh/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microwave-hydrothermal</td>
<td>100–200 (SEM)</td>
<td>39</td>
<td>Acetylene black</td>
<td>89 at 1/20 C</td>
<td>[18]</td>
</tr>
<tr>
<td>Ball milling and thermal heating</td>
<td>240 (laser diffraction)</td>
<td>31.7</td>
<td>Acetylene black</td>
<td>140 at 1/45 C 45 at 1 C</td>
<td>[23]</td>
</tr>
<tr>
<td>Liquid phase using oleic acid and oleylamine</td>
<td>7 (TEM): 40–125 (TEM)</td>
<td>25</td>
<td>Acetylene black</td>
<td>6 at 1/100 C 65 at 1/100 C</td>
<td>[24]</td>
</tr>
<tr>
<td>Liquid phase using oleic acid and oleylamine</td>
<td>17 (TEM)</td>
<td>25</td>
<td>Acetylene black and carbon nanofiber (VGCF)</td>
<td>153 at 1/100 C 62 at 1/2 C</td>
<td>[20]</td>
</tr>
<tr>
<td>Sol–gel</td>
<td>140 (SEM)</td>
<td>20</td>
<td>Acetylene black</td>
<td>134 at 1/100 C 81 at 1 C</td>
<td>[13]</td>
</tr>
<tr>
<td>Polyol</td>
<td>30 (TEM)</td>
<td>20</td>
<td>Carbon black</td>
<td>145 at 1/20 C 113 at 1 C</td>
<td>[15]</td>
</tr>
<tr>
<td>Ionothermal</td>
<td>300 (SEM)</td>
<td>17.6</td>
<td>Ketjenblack and sucrose</td>
<td>95 at 1/20 C (without CCCV test)</td>
<td>[19]</td>
</tr>
<tr>
<td>Hydrothermal</td>
<td>150–600 (SEM)</td>
<td>16.8</td>
<td>Acetylene black</td>
<td>126.7 at 1/100 C 113 at 1/10 C</td>
<td>[17]</td>
</tr>
<tr>
<td>Ultrasonic spray pyrolysis</td>
<td>10–50 (TEM)</td>
<td>16</td>
<td>Acetylene black</td>
<td>120 at 1/20 C 70 at 1 C</td>
<td>[12]</td>
</tr>
<tr>
<td>Liquid phase using oleic acid and oleylamine</td>
<td>10–20 (TEM)</td>
<td>10</td>
<td>Carbon black</td>
<td>165 at 1/40 C 66 at 1 C</td>
<td>This work</td>
</tr>
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</table>
We are currently investigating the influence of the quality of carbon additives on the optimization of cathode preparation, and on the capacities at higher C-rates.

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References