Preparation and Electrochemical Properties of LiMnPO$_4$
Cathode Material with Controllable Morphology

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Abstract. The morphology of particles was a really vital parameter influencing the electrochemical properties of LiMnPO$_4$ based cathode materials. In this work, nano-sized LiMnPO$_4$ with various kinds of morphology were prepared by solvothermal method. Then the phase structure, micro morphology and electrochemical properties were deeply analyzed by using XRD, SEM, electrochemical workstation and battery test system. The results indicated that obtained samples with porous and spindle-shaped powders show the best electrochemical properties, contributing to the decrease of Li$^+$ diffusion coefficient and enhancement of wetting properties between the active powders and the electrolyte.

1. Introduction

Due to the advantages of large energy density, long cycling lives, big output power density and excellent safety properties, rechargeable lithium-ion batteries (named as LIBs) had been extensively used as the power and energy reserve devices for electric vehicles, networks and other industrial applications. Generally, LIBs consist of cathode, anode, separator and electrolyte. Cathode electrodes often considered to directly influence the electrochemical properties, prices and security risks of LIBs, and are considered the key part of the batteries. Accordingly, many efforts have been played on the improvement for cathode electrodes in LIBs [1].

Layered structure LiCoO$_2$, olivine type LiFePO$_4$ and spinel structure Li-rich oxides cathode materials have been widely used and fully researched. Among them, polyanionic LiMnPO$_4$ has been thought as an exciting negative electrode in the reason for their extremely structure stabilization coming from strongly combined phosphorus and oxygen covalent bond [2]. Besides, LiMnPO$_4$ shows the merits in aspect of little money spent, small environmental pollution and cheap raw materials for preparation. Moreover, high energy density (700 Wh/kg) and high theoretical capacity (170 Ah/kg) are also attracted many attentions of researchers [3-4]. Therefore, LiMnPO$_4$ had been considering as a newly developed positive electrode materials for LIBs. Nevertheless, the weakness of this materials is also obviously on the poor conductivity of electronics and slow diffusion of Li ion in the host materials, which influencing the further using of LIBs in many situations [5]. Many methods had been introduced to enhance the properties of LiMnPO$_4$.

Particle size was firstly found to exist the huge influence for the electrochemical properties of LiMnPO$_4$ based cathode powders. The impact of grain scale for the stabilization of micro crystal structure during charging process of lithium manganese phosphate was discussed by Kim et al. [6], and...
they confirmed that the structure change of lithium manganese phosphate-based cathode powders might change along with particle diameter. It had been confirmed that nano sized particle size was helpful to raise significant infiltration between lithium manganese phosphate electrode and liquefied electrolytes, further to improving the power capabilities of the battery. The particles with little diameter often thought to help to reduce the diffusion path of lithium ion at the surface of the grain, led to a bigger capability at bigger charge/discharge electric currents, resulting great power capabilities [7]. Nanocrystalline (100 nm) LiMnPO$_4$ cathode particles had been synthesized by Yeo .et al [8] using a hydrothermal method. The cathode nanocrystalline exhibited the largest specific capacities of 153 mAh per gram for the initial cycle and 146 mAh per gram during 110 cycles, respectively. However, if the grain size continuous decrease, it was found that it could decrease the tap density during the preparation process [9]. Therefore, it is very harmful to apply this material-based electrode in large application of LIBs.

Except size effect, the morphology of particles is as well the significant parameter affecting electrochemical properties of LiMnPO$_4$ cathode powders. The anisotropy during Li$^+$ disinsertion and insertion process in LiMnPO$_4$ makes it very sensitive to the morphology of particles. Choi et al. [10] synthesized nano sized lithium manganese phosphate plates with olivine type structure and the thickness was about 50 nm by a novel solid-state reaction. This prepared LiMnPO$_4$ active material expressed the capacity achieving up to 167 mAh per gram. Then highly fragmented plate-like LiMnPO$_4$ powders were prepared by Zhen et al. using hydrothermal method [11]. The thickness of this prepared plate was about 100 nm. Their good electrochemical properties were attributed to its big ratio of exposed lattice plane on (0 1 0) and also the slight thickness directing the [0 1 0] direction.

In this work, nano-sized LiMnPO$_4$ with various kinds of morphology was synthesized by solvothermal method. Different solvents and the temperature were used to change the powder morphology. Then the phase, micromorphology and electrochemical properties were analyzed by XRD, SEM, electrochemical workstation and battery test system.

2. Experimental section

2.1 Preparation

LiMnPO$_4$ cathode powder was synthesized by the solvothermal method. All used reagents were analytically pure and commercially available, obtained from Fuyu Chemical Company and applied as raw powders without any treatment. Lithium hydroxide, manganese carbonate and phosphoric acid were applied as the raw reagents with the suitable ratio of 3/1/1. To investigate the controllable morphology of the LiMnPO$_4$ architecture, parallel experiments were conducted by keeping all the parameters constant and only changing the kinds of solvothermal solvent.

Firstly, $\text{H}_3\text{PO}_4$ and MnSO$_4$ was thoroughly dissolved in deionized water to obtain the solution with 1 mol/L. Then LiOH water solution (3 mol/L) was introduced into the mix $\text{H}_3\text{PO}_4$ and MnSO$_4$ contained solution drop by drop with strongly stirring for about 0.5 h. Ammonia solution was introduced drop by drop to adjust the pH-value of the prepared solution to 7. Then the mixed solution was dumped into an autoclave with volume of 100 mL, and treated at different temperature for twelve hours. After reaction, the resultant precipitations were collected and staved in baking oven at ninety degree for twenty-four hours. Then specimens with only water solution treated at 180 °C, with ethylene glycol (EG) at 180 °C, with ethylene glycol (EG) and citric acid (CA) mixture solution treat at 180 °C, 200 °C and with CA treated at 200 °C, were named as LMP, LMP-EG, LMP-EG-CA180, LMP-EG-CA200 and LPM-CA, respectively.

The prepared active samples were then blended with conductive agent (AC), PVDF in the weight ratio of 8/10/10 with NMP to obtain a cathode slurry by strongly grinding about four hours. Then prepared cathode slurry was printed on the surface of aluminum foil and heat-treated at 120 °C in a vacuum oven last for 24 hours with the aim to volatilize the NMP. Then, oven-dried active electrodes were cut into circular planchet with diameter about 30 mm. After that, the prepared electrodes were dried in the vacuum oven for 6 hours again in a vacuum oven, and then uses to assemble to the coin-type
battery cells. During the batteries making process, metal type Li, Celgard 2400 membrane and 1 M lithium hexafluorophosphate solution were used as anode electrode, separator and liquefied electrolytes, respectively. Finally, the coin batteries (CR-2032) were fabricated in the glove compartment filled with Ar gas (Mikrouna, Super, China).

2.2 Characterization
Micro grain structures of the obtained cathode materials were carried out by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) using Kα radiation of copper with the speed about 0.04 °/s over a 2θ range of 25-75 °. Scanning electron microscope (SEM, 7500F, Jeol, Japan) was applied to observe the surface appearance of the prepared active material.

Electrochemical impedance spectra (EIS) was carried out by the electrochemical workstation (CHI630E, Chinstruments, China) to discuss the resistance of the active material under the AC voltage at five millivolt and the test frequency range from 10² Hz to 0.1 MHz. The electrochemical properties of the prepared coin cells were tested by the battery measurement system (CT2001A, Land, China) under the voltage range of 2.3 to 4.4 V undergone different rates. In this work, 1C was defined as 170 mA/g. The cycling measurement was carried out at room temperature and the charge/discharge properties were tested under the similar rate ranging from 1/10 C to 5 C.

3. Results and discussion
Figure 1 displays the XRD patterns of lithium manganese phosphate series samples prepared with various solvents. Standard spectrum of LiMnPO₄ (JCPDS, No: 33-0804) is also shown in the bottom of the figure 1. It can be found that the obtained powders with olivine-type structure in the orthorhombic space were clearly observed. These results are well consistent with the reported works [12-13]. This means the obtained LiMnPO₄ powders are pure and does not exist any extra impurity peaks. On the other hand, the characteristic diffraction peaks are very sharp indicate that prepared powders with high crystallinity. According to the phase structure in figure 1, we can infer that solvothermal synthesis may synthetize olivine powder materials in single-phase with different solvent without calcination. The results also indicate that the kinds of solvent express little effects on the phase structure of LiMnPO₄ powders by using solvothermal synthesis method.

![XRD patterns of prepared LiMnPO₄ cathode powders.](image)

**Figure 1.** XRD patterns of prepared LiMnPO₄ cathode powders, LMP (A), LMP-EG (B), LMP-EG-CA180 (C), LMP-EG-CA200 (D) and LPM-CA (E), respectively.

Figure 2 is the SEM pictures of prepared LiMnPO₄ cathode powders. It can be found that the morphology is obviously different as the synthesis conditions changed. When the solvent is only deionized water, the prepared powders are rectangular shape and about 10 μm. And some nanoscale small particles are attached at the surface of big particle. These pellets which have inconsistency size.
unevenly distributed, as shown in figure 2(A). Then, ethylene glycol (EG) was introduced into the solvent, the particle size becomes much small (500 nm) with uniform distribution, as shown in figure 2(B). This indicates that EG is helpful to decrease the particle by using solvothermal method.

When the mixture solution of ethylene glycol (EG) and citric acid (CA) was used as the solvothermal solvent, porous and spindle-shaped powders appeared. In addition, as can be seen in figure 2 (C) and (D), this morphology does not change as the treatment temperature increased from 180 to 200 °C. This porous structure may help to decrease the lithium ion diffusion length and enhance wetting properties between cathode powders and the liquefied electrolytes, further enhancing the electrochemical properties of the batteries as discussed in the following. However, if only citric acid (CA) is used in the solution, the powders are rod-shaped with the diameter is about 200 nm, as shown in figure 2(E).

![Figure 2](image_url)

Figure 2. SEM pictures of prepared cathode powders lithium manganese phosphate. (A) LMP, (B) LMP-EG, (C) LMP-EG-CA180, (D) LMP-EG-CA200 and (E) LPM-CA, respectively.

Figure 3 shows the rate capabilities of all samples. The batteries are firstly tested at 1/10 C, then charged/discharged at 1/2 C, 1 C, 2 C and 5 C, respectively, finally cycled at 1/10 C again. Obviously,
electrode with LMP-EG-AC200 shows the great rate capacity, and in different rate the discharge capacity is 141.8, 122.5, 116.8, 107.9, and 92.6 mAh/g, respectively. The rate capabilities of samples LMP-EG-AC200 and LMP-EG-AC180 are almost the same in different rate. This may attribute to the similar morphology of these two samples. However, sample LMP expresses the worst rate performance. Then the cycle performances are tested in 1 C for 100 cycles, as shown in figure 3 (B). Among all samples, LMP-EG-AC200 expresses the highest and most outstanding discharge properties and still maintains to 94.6 mAh per gram. That is means, the loss of discharge capacity is about 19.5%. However, the discharge capacities for LMP, LMP-EG, LMP-EG-AC180, LMP-EG-AC200 and LMP-AC are 26.1, 62.6, 79.6, 94.7 and 47.2 mAh per gram after 100 cycling. Based on calculation in figure 3 (B), the retentions of capacity are 57.6%, 69.1%, 70.9%, 80.55 and 61.8%, respectively.

![Figure 3. Rate capabilities (A) and cycle performances (B) of various samples with different morphology.](image)

Electrochemical impedance spectra (EIS) tests were applied to analyze the electrochemical properties arising in active material/electrolyte interfaces. Also, in inside of the lithium manganese phosphate, the intercalation/de-intercalation behavior of lithium ion can be discussed by EIS. The EIS plots of these obtained cathode materials are shown in figure 4(A). It is obviously that the Nyquist curve contains two parts curves. Firstly, there is a quasi-semicircle at the frequency range from high to middle. In this range, the intercept at the real part axis in the high frequency area is considered as the ohmic resistance (Re) in liquefied electrolytes. Secondly, at the low-frequency range, there is a straight sloping line according to the Zw. The semicircles in the middle-frequency area are often considered as the charge transfer resistance [4, 14-16]. It can be found that the Re are close to each other (about 8-10 Ω), because of all the electrolyte of the batteries are the same. However, the Rct is obviously different. The sample LMP shows the largest Rct as high as 398 Ω, while the sample LMP-EG-CA200 shows the lowest Rct as 122 Ω. Moreover, the sample the Rct of samples LMP-EG-CA180 and LMP-EG-CA200 are almost the same. It is well known that the Rct is corresponds to the transfer transversion of active charge during the charge/discharge process of LiMnPO₄. The samples LMP-EG-CA180 and LMP-EG-CA200 with porous and spindle-shaped may help to enhance the wetting properties between the active powders and the electrolyte. Therefore, these samples show the low Rct.

On the other hand, based on the number of electron transport (n) and the concentration of lithium ions (C) during the electrochemical reactions in the active electrode, diffusion coefficient of Li⁺ (D_{Li}) often obtained by the formula as shown in following [4, 12, 16],

\[
D_{Li} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}
\]

here, R, T, A and F are constant, representing the gas state constant, temperature, effective working area, and Faraday constant, respectively. Besides, σ is often considered with sloping line which can be
calculated based on the plot slope of $Zr$ vs $\omega^{-1/2}$, and also considered as the Warburg factor, as shown in figure 4(B). It can be inferred that the sample LMP-EG-CA200 shows the largest diffusion coefficient, while the smallest diffusion coefficient is obtained for sample LMP. As shown in figure 2, the sample LMP-EG-CA200 shows the porous and spindle-shaped morphology, helping to decrease the diffusion length of Li$^+$. 

![Figure 4](image.png)

Figure 4 (A) Electrochemical impedance spectra of samples LMP, LMP-EG, LMP-EG-CA200, LMP-EG-CA180 and LMP-CA. (B) And line relationship of real part of impedance and $\omega^{-1/2}$ in low frequency of the obtained powders.

4. Summary
In this work, nano-sized LiMnPO$_4$ with various kinds of morphology were prepared by solvothermal method. All the samples were attributed to the orthorhombic olivine-type structure. The porous and spindle-shaped powders could be obtained by using ethylene glycol and citric acid mixture solution. the samples LMP-EG-AC200 expressed the highest discharge capacities as 141.8, 122.5, 116.8, 107.9 and 92.6 mAh/g at different rate of 1/10 C, 1/2 C, 1 C, 2 C and 5 C, respectively. These improvements were contributed to the well-developed porous and spindle-shape and decrease of Li$^+$ diffusion coefficient.

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