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Rational design of the micron-sized particle size of LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ cathode material with enhanced electrochemical performance for Li-ion batteries

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Abstract

Recently, micron-sized LiMn$_{1-x}$Fe$_x$PO$_4$ cathode materials have attracted attention due to its better rate capability and higher tap density than the nano-sized ones. However, the influence of the particle size on the energy density of micron-sized LiMn$_{1-x}$Fe$_x$PO$_4$ is still unknown. In this paper, we report the optimal particle size of the micron-sized LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ with enhanced electrochemical performance as cathode material in lithium-ion batteries (LiBs). The LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ sample with the particle size of ~9.39 μm delivers the initial discharge capacity of 124 mAh g$^{-1}$ at 0.2 C rate with high capacity retention of 94.35% after 100 cycles, which is higher than that with the particle sizes of ~2.71 μm, ~3.74 μm, ~6.41 μm or ~16.31 μm. This structure with the specific capacity of 122 mAh g$^{-1}$ at 0.5 C rate and 106 mAh g$^{-1}$ at 3 C rate also exhibits excellent rate performances. The improved electrochemical performances are mainly derived from its fast Li$^+$ diffusion, which causes the higher ionic conductivity. The LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ sample with the particle sizes of ~9.39 μm also shows the highest tap density (0.68 g cc$^{-1}$) among the as-prepared samples. This finding provides a new way to enhance the energy density of other cathode materials.

1. Introduction

Nowadays, the development of rechargeable lithium-ion batteries (LiBs) with better rate capability, longer cycling life and higher energy density is of great interest to accommodate the applications in more powerful plug-in hybrid vehicles or electric vehicles [1–7]. LiMnPO$_4$, as a new olivine structural material, has been widely studied due to its higher theoretical energy density of 684 Wh kg$^{-1}$ compared to the commercial LiFePO$_4$ (LiFePO$_4$: 578 Wh kg$^{-1}$) [3, 8–12]. However, the inherently low electronic and ionic conductivities of LiMnPO$_4$ (<10$^{-10}$ S cm$^{-1}$) make it with poor rate capability which limits its practical application [13, 14]. Great efforts have been dedicated to improve the rate capability of LiMnPO$_4$, like Mn-site doping, reducing the particle size to nano-size or carbon coating [10, 15–20]. Previous studies have shown that nano-sized LiMn$_{1-x}$Fe$_x$PO$_4$/C could greatly improve the rate capability but at the expense of low tap density [5, 15, 19–23]. What’s worse, the large specific surface area of nano-sized LiMn$_{1-x}$Fe$_x$PO$_4$ materials causes a series of undesired side effects, leading to poor cycling performance and safety hazard [21]. Recently, experimental investigations have demonstrated that micro-sized spherical morphologies were beneficial for the high tap density and high rate performance, especially the two-step sintering process to prepare the micro-sized LiMn$_{1-x}$Fe$_x$PO$_4$ [1, 21, 24]. Liu et al adopted a two-step sintering method with sucrose as the carbon source to get high volume energy density of 801.5 Wh l$^{-1}$ with tap density of 1.4 g cc$^{-1}$ [25]. Mi et al synthesized the LiMn$_{0.4}$Fe$_{0.6}$PO$_4$/C micro-spherical samples with 2% MWCNTs as the inorganic carbon source in the second sintering process, which delivers a capacity of
163.3 mAh g\(^{-1}\) at 0.1 C [14]. Whereas, to the best of our knowledge, the influence of the micro-sized particle size on the electrochemical performance and tap density of the LiMn\(_{1-x}\)Fe\(_x\)PO\(_4\) compound have few been studied. Here we reported the two-step sintering method to synthesis the LiMn\(_{1-x}\)Fe\(_x\)PO\(_4\) material with x = 0.2, which was considered as the best molar ratio for high rate capacity [15, 17]. By controlling the ball-milling time before the second-step sintering process, micro-sized LiMn\(_{0.8}\)Fe\(_{0.2}\)PO\(_4\) (LM\(_{0.8}\)F\(_{0.2}\)P) with different particle sizes were obtained, which were confirmed by the SEM and laser particle sizer. The electrochemical performances and the tap density of LM\(_{0.8}\)F\(_{0.2}\)P samples with different particle sizes were demonstrated.

2. Experimental section

2.1. Preparation of materials

Micro-sized LM\(_{0.8}\)F\(_{0.2}\)P samples with different particle sizes were synthesized via a two-step sintering method. All of the chemicals were used as received without any pretreatment or further purification. The mixture aqueous solution of 1 M LiH\(_2\)PO\(_4\), 0.8 M MnC\(_2\)O\(_4\)•2H\(_2\)O and 0.2 M FeC\(_2\)O\(_4\)•2H\(_2\)O were ball-milled for 6 h. After the spray drying process, the mixtures were transferred to a tube furnace and heated at 400 °C for 4 h under a N\(_2\) atmosphere to remove the moisture and preliminary phase. After the furnace cooled to room temperature naturally, the first-sintered mixture, PEG1500 (as a dispersant), Super P (SP) and sucrose to adjust the carbon content of the final products to about 3.6 wt% were ball-milled in ethanol. After the same ball-milling speed condition with different ball-milling times (15 h, 12 h, 9 h, 6 h and 3 h), the milled mixtures were dried and then treated with the second-step sintering process at 675 °C for 15 h under a N\(_2\) atmosphere. The final products are denoted as LM\(_{0.8}\)F\(_{0.2}\)P-2, LM\(_{0.8}\)F\(_{0.2}\)P-3, LM\(_{0.8}\)F\(_{0.2}\)P-6, LM\(_{0.8}\)F\(_{0.2}\)P-9 and LM\(_{0.8}\)F\(_{0.2}\)P-16, respectively, in ascending order of the final particle sizes of the LM\(_{0.8}\)F\(_{0.2}\)P sample as discussed below.

2.2. Characterization

XRD (MXP1HF, Mac Science Co. Ltd, Japan) was used to characterize the structure of the final LM\(_{0.8}\)F\(_{0.2}\)P samples with Cu K\(_\alpha\) radiation. The morphologies of the LM\(_{0.8}\)F\(_{0.2}\)Psamples were investigated using the field emission SEM (FESEM, JSM-6700F, JEOL). Particle size distribution was determined by the laser particle sizer (LS-POP6). The carbon content of the LM\(_{0.8}\)F\(_{0.2}\)P samples was measured on a high frequency infrared carbon and sulfur analyzer (model CS-901B). The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method (Micromeritics, ASAP 2020M). Tap density of all materials were measured by Tap denser (KYT-4000, JS Tech, Korea).

The electrochemical performance of LM\(_{0.8}\)F\(_{0.2}\)P samples was evaluated by galvanostatic cycling using CR2016-type coin cells. The lithium metal was chosen as an anode material and the Celgard 2400 film was used as the separator. The cathode materials was prepared by mixing LM\(_{0.8}\)F\(_{0.2}\)P, conductive carbon black (Super P) and polyvinylidene fluoride (PVDF) with a weight ratio of 8/1/1 in N-methyl-2-pyrrolidone (NMP) solvent. After grinding well, the viscous slurry was coated onto Al foils and dried at 80 °C for 12 h in vacuum. A mixture of ethylene carbonate (EC) and dimethyl carbonate (DEC) (volume ratio = 1:1) containing 1 M LiPF\(_6\) was used as the electrolyte. All cells were assembled in an argon-filled glove box (<0.1 ppm of oxygen and water). The cycle-life tests the cathodes were measured by a battery testing system (Neware BTS) at a current density of 0.2 C rate (1 C = 170 mA g\(^{-1}\)) between 2.5 and 4.3 V versus Li/Li\(^+\) at room temperature. The rate capability tests were performed within the voltage range of 2.5 V–4.3 V. During the experiment, the cells were charged to 4.3 V under a constant current - constant voltage (CC-CV) protocol at 0.2 C (1 C is equal to 170 mA g\(^{-1}\)) firstly, held at 4.3 V until the current decreased to 0.01 C, and then discharged at various rates (0.2C, 0.5C, 1C, 2C and 3C) to 2.5 V. Cyclic voltammetry (CV) scanning was performed on a CHI660C electrochemistry workstation in the voltage range of 2.5–4.6 V (versus Li/Li\(^+\)) from 0.05 mV s\(^{-1}\) to 0.4 mV s\(^{-1}\) scan rates. Electrochemical impedance spectroscopy (EIS) measurements were conducted on the same electrochemistry workstation by applying an AC voltage of 5 mV amplitude in the frequency range from 10 MHz to 100 kHz. During the EIS tests, the batteries were all at the 0% SOC (state of charge). All the electrochemical measurements were carried out at room temperature.

3. Results and discussion

XRD was utilized to characterize the crystal structure of the as-prepared LM\(_{0.8}\)F\(_{0.2}\)P samples. Figure 1 shows the XRD patterns of the final LM\(_{0.8}\)F\(_{0.2}\)P samples with different particle sizes. The five patterns were similar and all could be clearly indexed as olivine-type LM\(_{0.8}\)F\(_{0.2}\)P with a Pnmb space group of the orthorhombic system [22, 26, 27]. In addition, no diffraction peaks of crystalline carbon were detected, which indicated that the carbon in the LM\(_{0.8}\)F\(_{0.2}\)P samples was amorphous.
The cycle performance of all the LM₀.₈F₀.₂P samples at 0.2 C rate are presented in Figure 3. The capacity retentions of LM₀.₈F₀.₂P-2, LM₀.₈F₀.₂P-3, LM₀.₈F₀.₂P-6, LM₀.₈F₀.₂P-9 and LM₀.₈F₀.₂P-16 samples, which correspond to the different ball-milling times of 18 h, 12 h, 9 h, 6 h, 3 h, respectively. It can be seen that the LM₀.₈F₀.₂P sample with different particle sizes. All the samples exhibit two charge/discharge plateaus around 4.0 V and 3.5 V vs. Li/Li⁺, corresponding to the redox couples Mn³⁺/Mn⁴⁺ and Fe²⁺/Fe³⁺, respectively [17, 21]. Moreover, it is generally accepted that the large constant voltage ratio means the large electrochemical polarization. Table 2 presents the constant voltage ratios of the 1st cycle, the 10th cycle and the 80th cycles of the LM₀.₈F₀.₂P-2, LM₀.₈F₀.₂P-3, LM₀.₈F₀.₂P-6, LM₀.₈F₀.₂P-9 and LM₀.₈F₀.₂P-16 samples, respectively. For LM₀.₈F₀.₂P-2, LM₀.₈F₀.₂P-3 and LM₀.₈F₀.₂P-6 samples, smaller particles sizes are beneficial to shorten the lithium ion diffusion path resulting in small electrochemical polarization. But the large specific surface area (shown in Table 1) would extend the contact between LM₀.₈F₀.₂P-2, LM₀.₈F₀.₂P-3 or LM₀.₈F₀.₂P-6 samples and electrolyte, which caused the poor cycling performance (as shown in Figures 3(c) and (d)) [21]. For the LM₀.₈F₀.₂P-16 sample, the large particle size makes the Li⁺ diffusion path much longer, which caused the serious polarization phenomenon. The optimal particle size of the micron-sized LM₀.₈F₀.₂P-9 sample facilitates the fast diffusion of Li⁺, resulting in low constant voltage ratio.

The cycle performance of all the LM₀.₈F₀.₂P samples at 0.2 C rate are presented in Figure 3. The specific capacity is highly dependent on the micron-sized particle size. The initial discharge capacity is 115 mA h g⁻¹, 112 mA h g⁻¹, 123 mA h g⁻¹, 124 mA h g⁻¹ and 107 mA h g⁻¹ with the particle size of ~2.71 μm, ~3.74 μm, ~6.41 μm, ~9.39 μm and ~16.31 μm, respectively (shown in Table 1). After 100 cycles, their capacity retentions are 91.30%, 91.90%, 91.86%, 94.35% and 91.45%, respectively. It can be seen that the LM₀.₈F₀.₂P-9 sample with the particle size of ~9.39 μm shows better initial discharge capacity and higher capacity retentions than those with other particle sizes.

Figure 3(d) compares rate capability of LM₀.₈F₀.₂P sample with different particle sizes. Cells were charged to 4.3 V under a constant current - constant voltage (CC-CV) protocol at 0.2 C (1 C is equal to 170 mA g⁻¹) firstly, held at 4.3 V until the current decreased to 0.01 C, and then discharged at various rates (0.2C, 0.5C, 1C, 2C, and 3C) to 2.5 V. The figures of charge/discharge curves with different capacity are shown in Figure S3. It can be seen from Figure 3(d) that the rate performance of the as-prepared samples were greatly affected by the particle sizes. With the increase of the particle size from ~2.71 μm to ~9.39 μm, the enhancement of the rate capability was

**Figure 1.** XRD patterns of the LM₀.₈F₀.₂P-2, LM₀.₈F₀.₂P-3, LM₀.₈F₀.₂P-6, LM₀.₈F₀.₂P-9 and LM₀.₈F₀.₂P-16 samples, which correspond to the different ball-milling times of 15 h, 12 h, 9 h, 6 h, 3 h, respectively.
obtained in the LM0.8F0.2P samples. However, further increasing the particle size to ∼16.31 μm resulted in a decrease in capacity at all rates, which could be attributed to the long Li⁺ ion diffusion path through the micro-sized particles. Among the five as-prepared samples, the LM0.8F0.2P-9 one gives the best rate capability, which delivers a capacity of 122 mAh g⁻¹ at 0.2 C, 118 mAh g⁻¹ at 0.5 C, 113 mAh g⁻¹ at 1 C, 109 mAh g⁻¹ at 2 C and 106 mAh g⁻¹ at 3C respectively.

Analysis from the above results, we believe that the better electrochemical performance of LM0.8F0.2P-9 is mainly attributed to its improved ionic conductivity for the optimal particle size. Cyclic voltammetry (CV) scanning and electrochemical impedance spectroscopy (EIS) measurements were conducted to further verify the benefits of the optimal particle size.

As shown in figure 4, cyclic voltammograms (CV) curves of all samples at different sweeping rates (0.05, 0.1, 0.2, and 0.4 mV s⁻¹) between 2.5 and 4.6 V were recorded. The peak current (i_p) exhibits a well linear

Table 1. The particle size (D50), specific surface area (SSA) and tap density (TD) of the LM0.8F0.2P-2, LM0.8F0.2P-3, LM0.8F0.2P-6, LM0.8F0.2P-9 and LM0.8F0.2P-16 samples, respectively.

| Samples       | LM0.8F0.2P-2 | LM0.8F0.2P-3 | LM0.8F0.2P-6 | LM0.8F0.2P-9 | LM0.8F0.2P-16 |
|---------------|--------------|--------------|--------------|--------------|--------------|
| D50 (μm)      | 2.71         | 3.74         | 6.41         | 9.39         | 16.31        |
| SSA (m² g⁻¹)  | 39.46        | 37.73        | 36.31        | 31.56        | 8.43         |
| TD (g cc⁻¹)   | 0.57         | 0.65         | 0.62         | 0.68         | 0.58         |

Figure 2. SEM images of the (a) first-sintered LM0.8F0.2P precursor, (b) LM0.8F0.2P-16, (c) LM0.8F0.2P-9, (d) LM0.8F0.2P-6, (e) LM0.8F0.2P-3 and (f) LM0.8F0.2P-2 samples, respectively. With increasing the ball-milling time, the particle size decreased.
relationship with the square root of the scanning rate ($\sqrt{\nu}$) for each sample, which indicates that the reaction is controlled by the diffusion process. Besides, the oxidation or reduction peak position of LM0.8F0.2P is changed with the increased scan rate (figure 4), suggesting that the reaction is a quasi-reversible reaction. The diffusion coefficients of Li-ion ($D_{Li}$) were calculated using the Randles–Sevcik equation, which is applicable to the quasi-reversible reaction [3–5, 14].

$$i_p = 2.69 \times 10^5 ACD_{Li}^{1/2} n^{3/2} \nu^{1/2}$$

where $i_p$ is the peak current at different scan rates, $A$ is the active area of electrode (cm$^2$), $C$ is the initial concentration of Li ions in LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ (mol cm$^{-3}$), $D_{Li}$ is the apparent lithium ion diffusion coefficient (cm$^2$ s$^{-1}$), $n$ is the number of electrons per molecule in the redox process (n = 1), and $\nu$ is the potential sweeping rate (V s$^{-1}$). The active area of electrode is much larger than that of area of electrode and is difficult to measure accurately, which brings great uncertainty to the measurement of chemical diffusion coefficient in solid electrode by cyclic voltammetry. In our work, we chose the area of electrode during the whole calculation [5]. The obtained values of diffusion coefficient ($D_{Li}$) are listed in table 2. $D_{Li}$ of Li–Fe and Li–Mn correspond to the Fe and Mn redox reaction peaks respectively. All values are on the order of $10^{-10}$ to $10^{-9}$ cm$^2$ s$^{-1}$.

The lithium diffusion coefficients in the Fe redox regime are higher than that in the Mn redox regime for all samples, which indicates that the Li$^+$ transfer slower in the Mn regimes than in the Fe regimes. Furthermore, the

![Figure 3](image_url)
Figure 4. CV curves of (a) LM$_{0.8}$F$_{0.2}$P-2, (c) LM$_{0.8}$F$_{0.2}$P-3, (e) LM$_{0.8}$F$_{0.2}$P-6, (g) LM$_{0.8}$F$_{0.2}$P-9, and (i) LM$_{0.8}$F$_{0.2}$P-16 with corresponding plots of linear relationship between peak current ($i_p$) and square root of scan rate ($v^{1/2}$) at various sweeping rates (0.05, 0.1, 0.2 and 0.4 mV s$^{-1}$, respectively).
slight overlap of anodic and cathodic peaks represents a ‘more reversible’ reaction that can be associated with a single phase transition [28]. As shown in figure S4, the Fe redox reactions and Mn redox reactions in our as-synthesized LM0.8F0.2P-9 sample exhibited lower degrees of separation, which characterized a single phase transitions during lithiation/delithiation. Therefore, the LM0.8F0.2P samples in this work are solid solutions instead of a simple mechanical mixture of LiMnPO4 and LiFePO4 [28]. Therefore, the final diffusion coefficients should be a synergistically enhanced effect for the Fe regimes and the Mn regimes [5, 29–31]. Among these results, LM0.8F0.2P-9 shows the highest DLi of Li–Mn (3.25 × 10^{-9} cm² s^{-1}) and DLi of Li–Fe (4.17 × 10^{-10} cm² s^{-1}), which indicates that the LM0.8F0.2P-9 sample with the particle size of ~9.4 μm is beneficial for the improvement of the Li⁺ diffusion rate.

EIS was employed to further confirm the optimal particle size for the improvement of the electrochemical behaviors. As shown in figure 5, all the impedance plots consist of a depressed semicircle in the high-to-medium frequency region and a slopping line in the low frequency region. The straight line is attributed to the diffusion of lithium ions and the semicircle is related to the charge transfer between the electrolyte and the active material [4, 6, 23]. The impedance data was analyzed by fitting to an equivalent electrical circuit (inset). R_s and R_{ct} are the electrolyte resistance and lithium-ion intercalation charge-transfer resistance, respectively. CPE can be considered as the double-layer capacitance and the W_1 corresponds to the impedance of lithium-ions diffusion at the low frequency range [32]. The fitting results of R_s and R_{ct} are summarized in table 4. It can be seen that the charge-transfer resistance R_{ct} of LM0.8F0.2P-9 is 63.97 Ω, which is smaller than that of LM0.8F0.2P-2, LM0.8F0.2P-3, LM0.8F0.2P-6 and LM0.8F0.2P-16. The EIS results agree well with the electrochemical performance of the five LM0.8F0.2P samples, which indicates the Li⁺ ions can transfer more quickly on the interface of electrode/electrolyte.

Table 3. Apparent diffusion coefficients of Li⁺ (D_i) calculated from CV curves.

| Samples      | LM0.8F0.2P-2 | LM0.8F0.2P-3 | LM0.8F0.2P-6 | LM0.8F0.2P-9 | LM0.8F0.2P-16 |
|--------------|--------------|--------------|--------------|--------------|---------------|
| D_{Li} of Li–Mn (cm² s⁻¹) | 2.39 × 10⁻⁹ | 3.16 × 10⁻⁹ | 2.94 × 10⁻⁹ | 3.25 × 10⁻⁹ | 1.31 × 10⁻⁹ |
| D_{Li} of Li–Fe (cm² s⁻¹) | 2.21 × 10⁻¹⁰ | 2.36 × 10⁻¹⁰ | 1.91 × 10⁻¹⁰ | 4.17 × 10⁻¹⁰ | 4.14 × 10⁻¹⁰ |

Table 4. Summaries of the fitting results of electrolyte resistance (R_s) and lithium-ion intercalation charge-transfer resistance (R_{ct}) for LM0.8F0.2P samples.

| Samples      | LM0.8F0.2P-2 | LM0.8F0.2P-3 | LM0.8F0.2P-6 | LM0.8F0.2P-9 | LM0.8F0.2P-16 |
|--------------|--------------|--------------|--------------|--------------|---------------|
| R_s/Ω        | 17.52        | 20.05        | 13.18        | 11.97        | 9.39          |
| R_{ct}/Ω     | 101.80       | 78.74        | 67.63        | 63.97        | 78.00         |
4. Conclusions

We have successfully designed the micron-sized LM$_{0.8}$F$_{0.2}$P samples with different particle sizes by a two-step sintering method. The particle sizes had the obvious influence on the electrochemical performances of the LM$_{0.8}$F$_{0.2}$P samples. The LM$_{0.8}$F$_{0.2}$P-9 with the particle sizes of ~9.39 μm showed the best electrochemical performances: (i) the initial discharge capacity of 124 mAh g$^{-1}$ at 0.2 C rate with high capacity retention (94.35%) after 100 cycles; (ii) the discharge capacity of 122 mAh g$^{-1}$ at 0.5 C rate and 106 mAh g$^{-1}$ at 3 C rate. The LM$_{0.8}$F$_{0.2}$P-9 sample also showed the higher tap density (0.68 g cc$^{-1}$) than that with other particle sizes. The optimal particle size of the micron-sized LM$_{0.8}$F$_{0.2}$P cathode materials described in this work could be helpful for lithium ion batteries to achieve high energy density.

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