Nanoparticle shapes of LiMnPO$_4$, Li$^+$ diffusion orientation and diffusion coefficients for high volumetric energy Li$^+$ ion cathodes

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HIGHLIGHTS

- Rod-shaped, elongated and cubic nanoparticles of LiMnPO$_4$ were synthesized.
- The shape of LiMnPO$_4$ altered the 1D diffusion direction of Li$^+$.
- Particles with the shortest dimension along the b-axis possessed the highest D$_{Li+}$.
- The shape of LiMnPO$_4$ affected its tap density.
- The volumetric capacity of LiMnPO$_4$ increased via the formation of dense composite.

GRAPHICAL ABSTRACT
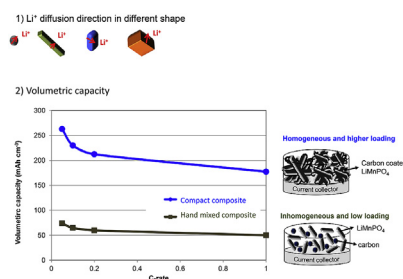
ABSTRACT

Nanoparticles of LiMnPO$_4$ were fabricated in rod, elongated as well as cubic shapes. The 1D Li$^+$ preferred diffusion direction for each shape was determined via electron diffraction spot patterns. The shape of nano-LiMnPO$_4$ varied the diffusion coefficient of Li$^+$ because the Li$^+$ diffusion direction and the path length were different. The particles with the shortest dimension along the b-axis provided the highest diffusion coefficient, resulting in the highest gravimetric capacity of 135, 100 and 60 mAh g^{-1} at 0.05C, 1C and 10C, respectively. Using ball-milling, a higher loading of nano-LiMnPO$_4$ in the electrode was achieved, increasing the volumetric capacity to 263 mAh cm^{-3}, which is ca. 3.5 times higher than the one obtained by hand-mixing of electrode materials. Thus, the electrochemical performance is governed by both the diffusion coefficient of Li$^+$, which is dependent on the shape of LiMnPO$_4$ nanoparticles and the secondary composite structure.

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1. Introduction

Energy storage systems are necessary when the electrical energy is produced excessively from renewable energy devices and to provide energy whenever needed. One of the promising methods to store energy is by using electrochemically rechargeable system such as Li-ion batteries.

Olivine structured materials, LiMPO$_4$ (M = Fe, Mn, Co, Ni) are well known to possess an excellent structural stability versus Li$^+$

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insertion/extraction. The covalent P-O bond strengthens the framework such that it does not collapse upon redox processes occurring at the transition metal ion $M^{2+/3+}$ [1]. This structural property of olivines provides the outstanding cyclability and thermal stability in the application of lithium ion batteries [2–6].

Among olivine materials, $LiFePO_4$ has been commercialized due to its facile synthesis and its higher electronic conductivity compared to other olivine materials. The drawback of $LiFePO_4$ is a low potential (3.6 V vs. Li^+/Li), leading to a maximum energy density of 578 Wh kg^{-1} (170 mAh $g^{-1} \times 3.6$ V). In contrast, $LiMnPO_4$ has a higher potential (4.1 V vs. Li^+/Li) with 171 mAh g^{-1} theoretical capacity, thus providing a potentially 20% higher energy density of 701 Wh kg^{-1} (170 mAh $g^{-1} \times 4.1$ V) than that of $LiFePO_4$. $LiCoPO_4$ and $LiNiPO_4$ have even higher cell potentials of 4.8 and 5.1 vs. Li^+/Li, respectively, but a lack of stable electrolytes at such high potentials, preventing their commercial application [7–9]. Thus, $LiMnPO_4$ is a strong candidate as cathode material for high energy Li-ion batteries.

To be used in a battery, $LiMnPO_4$ is also required to have good rate capabilities such as > 70% of theoretical capacity at 1C. A two-pronged approach in reducing the particle size of $LiMnPO_4$ on one hand and having a carbon coating on the surface of $LiMnPO_4$ particles on the other hand are most promising ways to obtain the high capacity due to the improvement of both ionic and electronic conductivity. Recently, Hatta et al. reported a high rate capability using pyrolytic carbon and Li_3PO_4 coating on rod shaped $LiMnPO_4$ nanoparticles, providing 160 and 145 mAh g^{-1} at 0.1C and 1C, respectively [10]. Platelet shaped $LiMnPO_4$ was reported to have a discharge capacity of 100 and 113 mAh g^{-1} at 1C at room temperature and 50 °C, respectively [4].

Furthermore, the Li^+ diffusion has to be controlled in the olivine materials. Olivines typically consist of slightly distorted LiO_6 and MO_6 octahedra and PO_4 tetrahedra in the crystal structure [1,11,12]. For $LiMnPO_4$ with space group $Pnma$, the Li^+ ion diffusion occurs in a zigzag-ed path along the b axis via edge sharing LiO_6 octahedra [13,14]. One way to improve the rate capability is thus to shorten the [010] diffusion path for Li^+ ion release and insertion. In addition, the exposure of the (010) facet on the surface of $LiMnPO_4$ particles can accelerate the kinetics of Li^+ in the $Pnma$ system [15–17]. Controlling the morphology and crystal size is thus vital for the battery performance as these parameters determine the preferred direction of the Li^+ diffusion channel and the shape of the particles [18,19].

To control the morphology and surface structure of $LiMnPO_4$ particles, synthetic parameters such as precursors, surfactants and solvents play an important role [4,20–24]. Obtaining $LiMnPO_4$ nanoparticles is however more difficult than for $LiFePO_4$. When the same synthesis method is applied to generate both, the particle size of $LiFePO_4$ is smaller than the one of $LiMnPO_4$ [25]. Various synthesis routes have so far produced morphologies of $LiMnPO_4$ with spherical [26], plate-shaped [4,27,28], rods [25,29,30], wires [31,32], microporous [33] and flower-like structures [34,35]. Their electrochemical properties were affected by different morphologies of $LiMnPO_4$ [36], which may have different orientations of Li^+ diffusion.

While one advantage of using nanoparticles is to improve rate capabilities [2,4,23,37–39], however, as their surface area is higher than the one of micron-sized particles, the volume of a nano-material composite is extremely high due to the empty space between the particles, resulting in a low tap density. This feature decreases the loading of nanomaterial on the specific area of the current collector and limits the volumetric energy density of nanomaterials based batteries. In case of $LiFePO_4$, the formation of micron-sized secondary particles increases the volumetric energy density compared to nanoparticles, increasing thus the tap density

of the composite. Liu et al. increased the tap densities of $LiMn_{0.4}Fe_{0.6}PO_4$ and carbon by the formation of a secondary microsphere composite prepared by spray drying [26]. For a micron-sized composite consisting of nano-$LiFePO_4$ and carbon, the volumetric discharge capacity increased was shown to increase by a factor of 2.5 compared to the one of nano-$LiFePO_4$ alone [40].

Therefore, there are a few challenges remaining for $LiMnPO_4$; 1) generating a desired shape of nano-$LiMnPO_4$ in a controlled way in order to facilitate Li^+ mobility, 2) improving the volumetric energy density of $LiMnPO_4$ nanomaterial without losing the high performance property of $LiMnPO_4$ and 3) optimising the specific capacity of this nano-$LiMnPO_4$, which is still a challenge probably due to the inhomogeneous mixing between agglomerated nanoparticles of $LiMnPO_4$ and carbon [35].

Although the particle shapes of $LiMnPO_4$ and their electrochemical performances were reported, Li^+ diffusion coefficients combined with the diffusion orientations were not further investigated in different shapes of particles. We present here a synthesis method based on thermal decomposition which allows us to obtain various sizes and shapes of $LiMnPO_4$ nanoparticles. The direction of the ionic diffusion (b-axis) in particles of various shapes was investigated using TEM electron diffraction in combination with the Li^+ diffusion coefficients ($\tilde{D}_{Li}$) on single particles. We furthermore examined the tap densities of various morphologies of nano-$LiMnPO_4$ and its composites with carbon. The volumetric and gravimetric capacities were further investigated with those materials.

2. Experimental

2.1. Chemicals

Manganese nitrate hexahydrate ($Mn(NO_3)_2 \cdot 6H_2O$), manganese acetate tetrahydrate ($Mn(CH_3COO)_2 \cdot 4H_2O$, >99%), manganese chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, >98%), lithium hydroxide monohydrate ($LiOH \cdot H_2O$, >98%), oleic acid ($C_8H_{15}COOH$, >99%), oleylamine ($C_9H_{17}NH_2$, >70%), citric acid ($C_6H_8O_7$, >99%) and solvents (benzyl ether, ethanol, hexane and N-methyl-2-pyrrolidone) were purchased from Sigma-Aldrich and Acros and used as received. Ketjenblack carbon, polyvinylidene fluoride (PVDF, $-(C_2H_2F_2)_n-$) and separators were supplied by Akzo Noble, Arkema Inc. in Philadelphia and Celgard in North Carolina, respectively.

2.2. Synthesis of $LiMnPO_4$

$LiMnPO_4$ material was prepared by the thermal decomposition method using oleic acid and oleylamine as surfactants and reducing agents. The detail experiments are described in our previous study [30]. To obtain the different shapes of nano-$LiMnPO_4$, 3 mmol of each manganese precursor ($Mn(NO_3)_2 \cdot 6H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$ or $MnCl_2 \cdot 4H_2O$) and $LiOH \cdot H_2O$ were dissolved in 9 or 27 mmol oleic acid ($C_8H_{15}COOH$) during heating until 120 °C. 20 ml of benzyl ether was added to the solution afterwards with continuous heating. 9 or 27 mmol oleylamine ($C_9H_{17}NH_2$) and 3 mmol H_3PO_4 were injected at 230 °C of the solution. The solution was stirred vigorously and kept at 230 °C for 1.5 h. Then the temperature was increased to between 265 and 280 °C for 1–4 h. After the reaction, the suspension was centrifuged to collect the sedimented dark brown powder. This material is rinsed with ethanol and hexane and then centrifuged.

A ligand-exchange method using citric acid aqueous solution was applied in order to remove the organic residue in as-synthesized $LiMnPO_4$ after rinsing [30]. The organic residue containing dark brown $LiMnPO_4$ powder turned to greyish white after the ligand-exchange.