



Nonaqueous synthesis of nano-sized $\text{LiMnPO}_4\text{@C}$ as a cathode material for high performance lithium ion batteries



Jingmin Fan^a, Yang Yu^a, Yang Wang^a, Qi-Hui Wu^b, Mingsen Zheng^{a,*}, Quanfeng Dong^{a,*}

^a State Key Lab. of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, China

^b Department of Chemistry, College of Chemistry and Life Science, Quanzhou Normal University, Quanzhou 362000 Fujian, China

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ABSTRACT

A nano-sized $\text{LiMnPO}_4\text{@C}$ core@shell structure was prepared through a facile two-step method. Oleylamine was introduced in the synthesis process using as both solvent and carbon source. The $\text{LiMnPO}_4\text{@C}$ structure has a particle size smaller than 40 nm with uniform 2–3 nm carbon coating layers, which interweave to form a secondary micrometer-sized mesoporous structure. The as-prepared $\text{LiMnPO}_4\text{@C}$ showed a high capacity of 168 mAh g^{-1} at 0.1 C and 105 mAh g^{-1} at 5 C applied as a cathode electrode for lithium ion batteries. The thin layer carbon coating not only increases LiMnPO_4 in electronic and ionic conductivity, but also enhances its cycling ability by stabilizing the solid electrolyte interface.

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1. Introduction

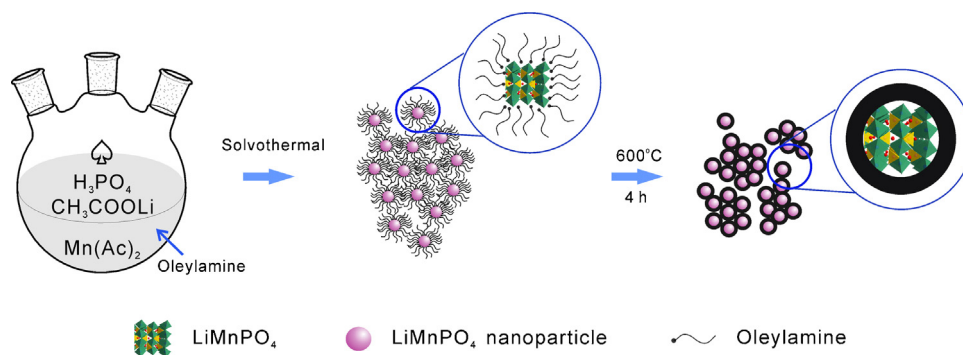
Compared with the commercially employed positive electrode materials such as LiCoO_2 , LiNiO_2 (layered structure), and LiMn_2O_4 (spinel structure), olivine-type lithium transition metal phosphates LiMPO_4 ($M = \text{Fe, Mn, Co, Ni}$) are considered as more promising cathode materials for lithium ion batteries (LIBs) used in electrical vehicles (EVs), plug-in hybrid electrical vehicles (HEVs), and green grids [1,2] because of the strong covalent bonding in PO_4^{3-} fundamental units that guarantees the high structural and thermal stability [3]. In the past two decades, LiFePO_4 has attracted much attention due to its performance of near-theoretical capacity and excellent cycling stability, which has induced it used in commercial productions [4,5]. Actually, other LiMPO_4 ($M = \text{Mn, Co, Ni}$) could offer much higher potentials than LiFePO_4 ($578 \text{ Wh kg}^{-1} = 170 \text{ mAh g}^{-1} \times 3.4 \text{ V} \times 1000$), which means that they can provide higher energy and power densities. For example, LiMnPO_4 (LMP) ($684 \text{ Wh kg}^{-1} = 171 \text{ mAh g}^{-1} \times 4.1 \text{ V} \times 1000$) was considered as the most promising cathode for 4 V-LIBs, which matches well with the presently used organic carbonate electrolytes.

However, the slow lithium extraction and insertion kinetics in LMP hindered its practical applications [6,7]. This was mainly caused by the fundamental properties of lithium manganese phosphate, for example, low electronic and ionic conductivities,

Jahn–Teller distortion of Mn^{3+} ions (in the charged state) [8–10], larger interface strain due to the larger volume change between LMP and MnPO_4 during intercalation/deintercalation of lithium (ca.10%) [11], and the metastable nature of the delithiated phase. Meligrana et al. [12] found that the specific capacity of LiFePO_4 was highly related to the surface area. Jeon and coworkers [13] coated LiFePO_4 particles with different mounts of carbon by adding sugar into the reaction system. Their results showed that particles coated with homogeneous carbon films could promote their discharge capacity close to the theoretical value. Similar rules were also found for LMP. Rangappa et al. [14] prepared three LMP materials with the particle size of 20, 60, and 100 nm, respectively. Electrochemistry measurements showed that the capacity increased with the size reducing. Yoshida et al. [15] also analyzed the size effect of LMP particles on the battery properties using scanning transmission electron microscopy-electro energy loss spectroscopy (STEM-EELS) who confirmed that the capacity improvement was contributed to the size reduction. The capacity and thermal stability enhancement of LMP resulted from the carbon coating was further proved by many works [16,17]. Moreover, the effective carbon content, uniformity of carbon coating, and the tight combination between carbon and the particles greatly influenced their electronic performance [18,19]. Wang et al. [20] synthesized LMP nanoplates and reported that carbon-coating via chemical vapor deposition (CVD) approach resulted in a significant improvement in the electrochemical performances compared to the ball milling process, because in the CVD process, the carbon-coating layers possess a more homogeneous surface morphology and a stronger adhesion force. Hence, combination of reducing particle size and uniformly carbon

* Corresponding authors.

E-mail addresses: qhwwu@qztc.edu.cn (Q.-H. Wu), mszheng@xmu.edu.cn (M. Zheng), qfdong@xmu.edu.cn (Q. Dong).



Scheme 1. Schematic drawing of an oleylamine-assisted solvothermal in-situ carbon coating approach for synthesis of nano-sized LiMnPO₄@C particles.

coating is an effective way to improve the electrochemical performance of LMP.

Various methods have been developed to prepare LMP nano-structures, such as sol-gel method, co-precipitation, mechano-chemical activation, spray technology, solid-state reactions etc. Unfortunately, few works have been achieved on synthesis of LMP materials with discharge capacity over 120 mAh g⁻¹ at 1C. Rui et al. [21] synthesized ultrathin (010)-oriented LMP nanosheets via liquid-phase exfoliation approach combined with a solvothermal approaches in supercritical fluids. But similar to other wet chemical methods, two drawbacks were hard to be overcome: 1) particles of LMP were usually large and nonuniform; 2) extra carbon-coating process are needed and the mass content of carbon often surpasses 20% due to the low coating efficiency [15,22]. The chemical synthesis of well carbon coated nano-sized LMP is thus desirable, but remains a significant challenge.

In our previous studies, we have successfully prepared nano-sized LiFePO₄@C with hierarchical structures using an oleylamine (OAm)-mediated solvothermal method [23]. OAm has been introduced as a capping agent in the synthesis of noble metal and metal oxide nanoparticles [24,25], and firstly reported by Honma's group [14] using as capping agent in preparation of LMP nanoparticles by controlling their crystallite size below 50 nm under a harsh supercritical fluid condition (SFC). In this work, through the facile OAm-mediated solvothermal method, we controlled the size of LMP particles smaller than 40 nm and successfully made tight and uniform carbon layers on their surfaces. During the solvothermal process OAm was absorbed on the surface of LMP and restrain the growth of the particle; after the following heating treatment, OAm was carbonized on the surface.

Thermogravimetric analysis (TGA) showed that the carbon content is about 7%. The prepared nano-sized LMP@C cathode electrode exhibited excellent electrochemistry performance. Under room temperature it nearly reached the theoretical capacity at 0.1C, which has not been reported before. The structure, morphology, electrochemical performance and the formation mechanism were subsequently studied. The function of the carbon coating layers was consequently discussed.

2. Experimental

Scheme 1 shows the synthesis process designed for preparation of LMP@C particles. H₃PO₄, CH₃COOLi and Mn(AC)₂ were used as the precursors for synthesis of LMP. In the first solvothermal procedure, OAm is adhered on the surface of the just formed LMP particles through a week bond, which inhibits their continuous growth. In this case the size of LMP particles is handily limited. Instead of removing the OAm from the surface by washing reported by other studies, we designed a subsequent sintering step to carbonize the OAm by forming a uniform carbon shell on the surface of LMP particles. The carbon layers of the primary particle contact with each other tightly, which consequently form a carbon network in the secondary micro-size particulate structure as indicated in **Scheme 1**.

In a typical synthesis process, Mn(CH₃COO)₂ (8 mmol) and CH₃COOLi·2H₂O (8 mmol) were separately dissolved in 20 mL anhydrous ethanol. The two ethanol solutions were mixed into a continuously stirring 250 mL three-neck flask for 30 min which was filled with 60 ml OAm at 105 °C in nitrogen atmosphere. Then H₃PO₄ (0.55 mL, ≥85%) anhydrous ethanol (5 mL) solution was

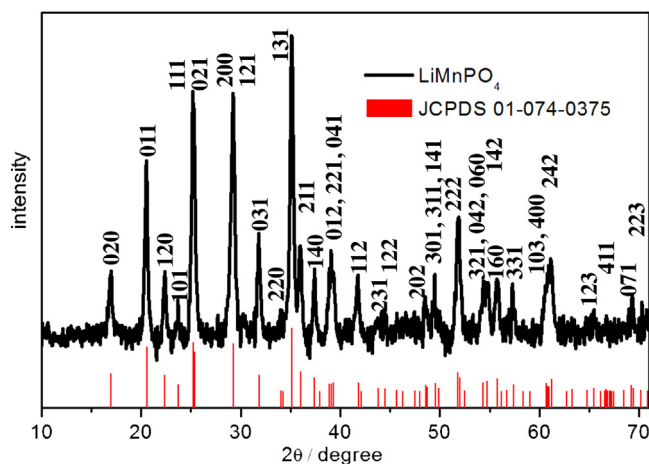


Fig. 1. X-ray diffraction pattern of the as-synthesized LiMnPO₄@C sample.

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