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Comparative study of $LiMnPO_4$/C cathodes synthesized by polyol and solid-state reaction methods for Li-ion batteries

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HIGHLIGHTS

- Effect of synthetic methods on LMP was investigated.
- LMP had 4–5% cation mixing from powder neutron diffraction data.
- TEM analysis showed that polyol method grows LMP platelets parallel to *bc*-plane.
- Polyol method with super-P composite offered the best performances.
- Capacity of LMP was strongly influenced by upper cut-off voltage used.

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ABSTRACT

A systematic comparison of LMP prepared by solid-state reaction (SSR) and polyol methods was carried out through detailed analyses that included: X-ray and neutron powder diffractions, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electrochemical characterization. The LMP synthesized by the two different methods had a similar amount of Li/Mn cation mixing, ca. 4–5%. The polyol method provided a flower-like morphology to the LMP particles, in the form of platelet of which growth direction is parallel to the *bc*-plane. The LMP prepared by the polyol method was further optimized by carbon composite using two different kinds of carbon sources: Shawinigan acetylene black (AB) and Super-P Li carbon black (SP). With the smallest crystallite size and a homogeneous carbon particle network, the LMP processed with SP delivered better cathode performance than both the AB – mixed LMP and that prepared by the SSR method. AC-impedance spectroscopy of the LMP composite with SP showed an abrupt increase in impedance after 50% delithiation. Because of this difficulty of charging, the capacity of the LMP composite with SP was strongly influenced by the upper cut-off voltage used.

1. Introduction

The olivine-structured $LiFePO_4$ (LFP) has emerged as a viable positive electrode material for Li-ion batteries [1]. It has demonstrated properties of safety, stability, and cyclability while having good specific capacity and energy density [1]. Intrinsically, LFP has the material characteristics of an insulator with low ionic ($\sigma_{ion} = 1.9 \times 10^{-9}$ S cm^{-1} at 147 °C along the *b*-axis) and electronic ($\sigma_{electron} \sim 7.5 \times 10^{-9}$ S cm^{-1} at 40 °C along the *a*-axis) conductivities [2]. Fortunately, two material innovations have been achieved that improve the potential for LFP to be a viable electrode material for electric vehicle (EV) applications: i) the use of carbon composites to improve electronic conductivity and ii) a reduction of the effective primary particle size to the nanometer regime to compensate for the low ionic conductivity. However LFP delivers a relatively low operating voltage of ~3.5 V (vs. Li^+/Li^0) compared with other positive electrode materials such as $LiCoO_2$ and $Li_{1+x}Mn_{2-x}O_4$. This remains a disadvantage of LFP and has motivated investigations into materials that have many of the positive aspects of the olivine system but with improved energy density and capacity.

$LiMnPO_4$ (LMP) offers a higher operating voltage of 4.1 V (vs. Li^+/Li^0) compared with that of LFP [3]. Fig. 1 illustrates the crystal

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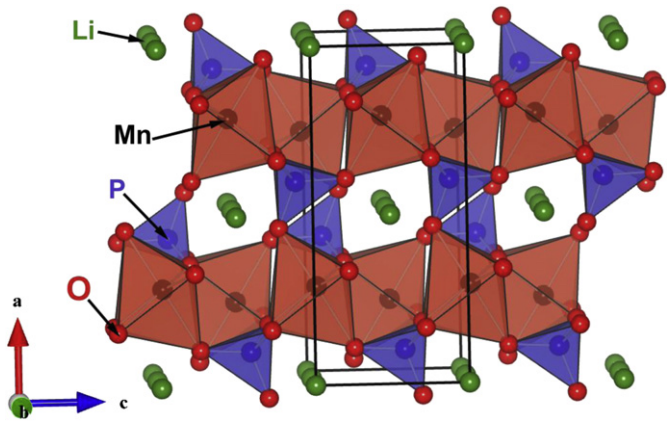

Fig. 1. Crystal structure of $LiMnPO_4$. Solid lines indicate a unit cell.

structure of LMP, which is orthorhombic, with a space group of *Pnma*, referred to as the olivine structure [3]. The crystal lattice of LMP consists of corner-sharing MnO_6 octahedra and edge-sharing LiO_6 octahedra that are linked by PO_4 tetrahedra. The Li^+ pathway in the olivine crystal structure of these materials is one-dimensional, parallel to the *b*-axis as seen in Fig. 1 [4]. LMP is an appealing alternative to LFP because it provides a higher operating voltage, and a ~20% higher gravimetric energy density as can be seen in Table 1 (along with the physical and electrochemical properties of LMP and those of LFP).

There are, however, additional challenges with LMP such as lower electrical conductivity and being less amenable to carbon coating methods compared to LFP [5]. For example, LMP has more difficulty in forming effective conductive carbon coatings due to the less reactive nature of Mn, relative to Fe, to carbon sources. It has been suggested that the rate limiting factor in LMP is low electrical conductivity rather than the ionic conductivity [4]. There are several approaches to improve the performance of LMP. An important approach is to reduce the crystallite size and modify the primary and secondary particle morphology so as to minimize the length of the Li^+ conduction channels [6]. An ideal morphology would have the shortest dimension along the *b*-axis. Control of crystal morphology and growth has been shown to be possible with soft-chemistry synthetic routes such as sol–gel, polyol, hydrothermal, and microwave synthesis [6–9]. Particularly attractive is the polyol method which allows the synthesis of inorganic nanoparticles without further heat-treatment [7]. Traditional solid-state synthesis routes also have been used to prepare LMP though these approaches provide limited control over particle size and morphology [10]. However, a solid-state synthesis route does the have the benefit of an easier scale-up than a polyol route. In this paper, two synthesis methods, a solid-state procedure and a polyol reaction, were explored to better understand the role of factors such as preparation method, particle size, and particle morphology have on the electrochemical performance of LMP.

Table 1
Comparison of $LiFePO_4$ and $LiMnPO_4$.

Properties	$LiFePO_4$	$LiMnPO_4$
Density (g cm^{-3})	3.7	3.4
Theoretical gravimetric capacity (mAh g^{-1})	170	171
Theoretical volumetric capacity (mAh cm^{-3})	629	581
Operation voltage (vs. Li^+/Li^0) (V)	3.45	4.1
Theoretical gravimetric energy density (Wh kg^{-1})	586	701
Theoretical volumetric energy density (Wh L^{-1})	2170	2384
Electrical conductivity (S cm^{-1})	$\sim 10^{-9}$	$<10^{-10}$

2. Experimental

2.1. Polyol synthesis method

LMP was formed via a modified polyol synthesis in which stoichiometric amounts of $Mn(CH_3COO)_2 \bullet 4H_2O$ (Mn-Ace) and LiH_2PO_4 (Sigma–Aldrich), were combined using ethylene glycol (EG) as the solvent. The EG acts both as a chelating agent and as a mild reducing agent to the Mn^{2+} ions. In a typical reaction, 150 mL of ethylene glycol is added to a 250 mL 3-neck round bottom flask with a condenser and stir-bar, and heated to 100 °C to which 0.03 mol of Mn-Ace was added and heated ~100 °C for 20 min. Formation of a deep ruby-colored solution indicated the complete dissolution of the Mn-Ace. 15 mL (0.03 mol) of a 1 M LiH_2PO_4 aqueous solution was then added drop wise under constant stirring conditions at a rate of less than 1 mL min^{-1} via a syringe. The mixture was heated at 135 °C, under reflux and constant stirring for 4 h. The final product was obtained by transferring the solution into centrifuge tubes which were centrifuged at 4000 rpm for 20 min. The supernatant was removed and the sediment was re-dispersed in ethanol and centrifuged again. This process was repeated until the supernatant was clear. The resulting gel was then filtered (0.8 μm Nylon Membrane Filters) and washed with ethanol followed with a final rinse of acetone. The remaining solid was then heated under vacuum at 120 °C overnight.

To attain any usable capacity from phosphate-based materials, particles must have layer of conductive carbon or be intimately embedded in a conductive carbon network. A number of ways to achieve this have been presented in the literature [11]. Among them, one of the most effective is high-energy ball milling of the LMP material with a carbon source. This method was adapted for this work [3]. Two carbon black sources were used: Shawinigan acetylene black (Chevron Philips Acetylene Black) (AB) and Super-P Li carbon black (Timcal) (SP). A 20 wt% ratio of carbon to LMP was used. The mixture was transferred to a stainless steel vessel for planetary ball milling with stainless steel balls, and a ball mass ratio of 5:1 was used. The mixture was milled at 300 rpm for 4 h.

2.2. Solid-state reaction synthesis method

LMP was also synthesized via a solid-state reaction method [10]. Stoichiometric amounts of Li_2CO_3, $MnCO_3$, and $(NH_4)_2HPO_4$ (Sigma–Aldrich) precursors were mixed with super-P carbon black (Timcal) (SP) to produce 2.5 g (0.0159 mol) of LMP with 20 wt% carbon. The carbon provides two functions: i) to provide the carbon source for the necessary conductive carbon network and ii) to limit phosphate particle growth during the synthesis. The precursors were loaded into a stainless steel vessel for planetary ball milling (80 mL) with stainless steel balls with reactants to ball mass ratio of 20:1. The container and contents were then subjected to high-energy ball milling in a Fritch planetary ball mill (Fritch 4000). The duration of this milling was 12 h at 300 rpm. The milled powder was collected and reground. The powder was then heated at 550 °C for 6 h in an Ar/3% H_2 atmosphere in a tube furnace (5 °C min^{-1} heating and cooling rate). The final material was of a mix of LMP particles embedded in a carbon network and no further carbon treatment was needed.

2.3. Material characterization

Powder X-ray diffraction (XRD) measurements were carried out with a Bruker D8 diffractometer with Cu-$K_{\alpha 1}$ radiation in Bragg-Brentano configuration. Powder neutron diffraction measurements were conducted at POWGEN diffractometer (beamline 11A) at the Spallation Neutron Source at Oak Ridge National Laboratory.