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$LiMnPO_4$ Olivine as a Cathode for Lithium Batteries

Zhumabay Bakenov[1,§] and Izumi Taniguchi[*,2]

[1] *Department of Chemical Engineering, Faculty of Engineering, University of Waterloo, Waterloo, Ontario, Canada*

[2] *Department of Chemical Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan*

Abstract: The olivine structured mixed lithium-transition metal phosphates $LiMPO_4$ (M = Fe, Mn, Co) have attracted tremendous attention of many research teams worldwide as a promising cathode materials for lithium batteries. Among them, lithium manganese phosphate $LiMnPO_4$ is the most promising considering its high theoretical capacity and operating voltage, low cost and environmental safety. Various techniques were applied to prepare this perspective cathode for lithium batteries. The solution based synthetic routes such as spray pyrolysis, precipitation, sol-gel, hydrothermal and polyol synthesis allow preparing nanostructured powders of $LiMnPO_4$ with enhanced electrochemical properties, which is mostly attributed to the higher chemical homogeneity and narrow particle size distribution of the material. Up-to-date, the $LiMnPO_4$/C composites prepared by the spray pyrolysis route have the best electrochemical performance among the reported in the literature.

Keywords: Spray pyrolysis, $LiMnPO_4$, lithium secondary batteries, cathode materials.

1. INTRODUCTION

Since Radhi *et al.* [1] first introduced $LiFePO_4$ olivine as a cathode for rechargeable lithium batteries, the olivine structured transition metal phosphates, $LiMPO_4$ (M= Co, Fe, Mn) have attracted tremendous attention of the researchers worldwide due to its low cost, nontoxic and environmentally friendly nature. In phospho-olivines, all of the oxygen ions form strong covalent bonds with P^{+5} to form the PO_4^{3-} tetrahedral polyanion and stabilize the entire three-dimensional framework, which provides improved stability and extreme safety under abusive conditions [2]. However, this structure restricts the electrochemical reaction kinetics in phospho-olivines due to the insulation effect of the polyanion. Therefore, almost a decade past before $LiFePO_4$ olivine cathode for lithium batteries was developed and successfully commercialized. There were systematic works of many research groups worldwide to adopt various processes and methods to overcome the main disadvantage of $LiFePO_4$ restricting its application, low electronic conductivity. Various methods have been applied, including different synthesis techniques, coating by a conductive layer of carbon [3-6] and dispersed metal particles [7], preparation of $LiFePO_4$/carbon composites [5, 8-11], producing smaller particles of cathode material [5, 7, 12]. Nowadays, $LiFePO_4$ cathode has become one of the main commercial cathode materials for lithium batteries.

The successful development of a high performance and environmentally safe $LiFePO_4$ cathode encouraged the great interest of researchers to another olivine structured cathode, $LiMnPO_4$, which is even more attractive than lithium iron phosphate because of its higher theoretical energy density due to the higher operating voltage of 4.1 V, which is comparable with that of the present $LiCoO_2$ cathode, and lies within the stability window of the common non-aqueous electrolytes. This advantage is especially important for the large scale applications, e.g. electric transportation and power back-up systems. There are several general review papers published recently on the cathode materials for lithium batteries including $LiFePO_4$ olivine [13-15]. Here, we would like to overview the recent publications on $LiMnPO_4$ cathode for lithium batteries by the authors of this manuscript and other groups. We would like to summarize the available literature data on this promising cathode and highlight the main problems and possible approaches to overcome them.

2. STUDIES ON HIGH-PERFORMANCE $LiMnPO_4$ OLIVINE CATHODE

Fig. (**1**) presents the schematics of the $LiMnPO_4$ olivine structure. $LiMnPO_4$ has an olivine structure, where Mn and Li occupy octahedral 4*c* and 4a sites, and P atom is in 4*c* site, respectively. The O atoms are in a hexagonal close-packed arrangement. The MnO_6 octahedra are separated by PO_4 polyanions that leads to the significant reduction of the electrical conductivity of the material. It results in a poor rate capability and a slow utilization of Li ions in the olivine host structure. Therefore, similarly to $LiFePO_4$, the successful preparation of high performance $LiMnPO_4$ cathode could be achieved through the preparation of the conductive composites of fine particles of this material. However, the current durability of Li_xMnPO_4 is orders-of-magnitude inferior to that of Li_xFePO_4 [16], which makes the preparation of the high conductive $LiMnPO_4$/C composites more difficult than in the case of the lithium-iron phosphate.

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*Address correspondence to this author at the Department of Chemical Engineering, Graduate School of Science and Engineering, Tokyo Institute of Technology, Tokyo, Japan; Tel/Fax: +81-3-5734-2155;
E-mail taniguchi.i.aa@m.titech.ac.jp

§Current Address: Nazarbayev University, School of Engineering, Astana, Kazakhstan

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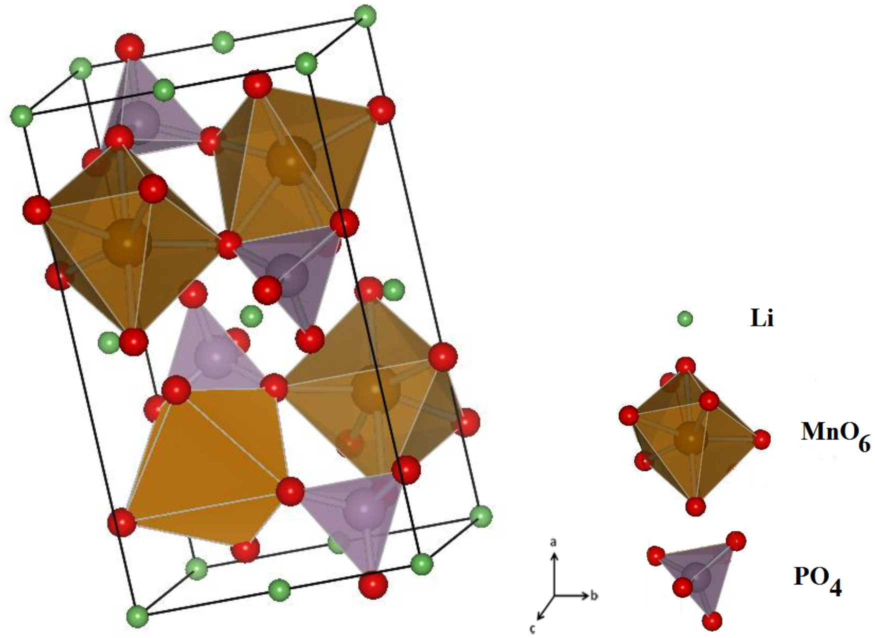

Fig. (1). Structure of the LiMnPO$_4$ olivine with *Pnma* space group.

Although there are tremendous efforts to develop a practical LiMnPO$_4$ cathode, only limited literature data on this cathode material for LIBs are available [17, 20-26]. There are several synthetic techniques applied to prepare LiMnPO$_4$/C composites. Carbon additives to synthetic precursors were first proposed by Ravet *et al.* [18]. Along with acting as a conductive agent, carbon prevents the oxidation of the electrochemically active species during heat treatment and prevents the particles agglomeration [19]. Li *et al.* [17] reported the preparation of the carbon-containing LiMnPO$_4$ compounds prepared using a solid-state reaction by adding carbon black to the synthetic precursors. All the samples were identified as LiMnPO$_4$ with an ordered olivine structure indexed by orthorhombic *Pnmb* space group. The defined lattice constants were a = 6.106(1) Å, b = 10.452(1) Å, and c = 4.746(1) Å. The synthesis temperature greatly affected the cathode performance and the samples synthesized at 500 °C had the greatest discharge capacity. The authors showed the reversible extraction-insertion of lithium into LiMnPO$_4$, which resulted in a flat plateau about 4.1 V *vs* lithium in charge-discharge profiles. The material exhibited an overall reversible capacity of 140 mAh g^{-1} at room temperature. The limiting factor in MnPO$_4$/LiMnPO$_4$ redox reaction is mostly its low ionic and/or electronic transport within the LiMnPO$_4$ particles rather than the slow charge-transfer kinetics [20]. This prevents the successful operation of the cathode at high charge-discharge rates and an acceptable discharge capacity could be achieved only at the low rate galvanostatic charge-discharge operation or in a constant current-constant voltage charge mode or trickle mode conditions when a higher charge state is achievable. Delacourt *et al.* [21] synthesized ~100 nm particles of LiMnPO$_4$ by precipitation, which delivered a reversible capacity of 70 mAh g^{-1} at 0.05C. Kwon *et al.* [22] prepared LiMnPO$_4$/C composite of 130 nm average diameter *via* a sol-gel method followed by dry ballmilling with a carbon source, which delivered a reversible capacity of 134 mAh g^{-1} at 0.1C. They showed that the smaller particles were more preferable for the higher C-rates. Fang *et al.* [23] prepared LiMnPO$_4$ by a hydrothermal method. The Mn^{2+} disorder on Li^{+} sites was depressed by increasing the synthesis temperature, and the highest discharge capacity achieved is 68 mAh g^{-1} at a current density of 1.5 mA g^{-1}. The increase in carbon content up to 50% during the ballmilling of the solid-state reaction prepared LiMnPO$_4$ improves the conductivity of material as well as destroys big agglomerates and allowed about 30% of the theoretical capacity at C/5 [24]. Wang *et al.* [25] reported a polyol synthesis of the platelet morphology of 30 nm thick LiMnPO$_4$. Using the trickle mode conditions, they achieved a discharge capacity of 141 mAh g^{-1} at 0.1C at room temperature. LiMnPO$_4$ nanoparticles synthesized by the same method exhibited a discharge capacity of about 140 mAh g^{-1} at 0.1C under the trickle mode conditions [26]. Irrespective to the preparation technique, in order to prepare a conductive composite, the most of works above used post-synthesis ballmilling of the LiMnPO$_4$ powders with carbon.

The partial substitution of Fe for Mn in LiFe$_{1-x}$Mn$_x$PO$_4$ was considered to improve the cathode electrochemical performance [27-29]. These compounds have two voltage regions of the electrochemical activity corresponding to the redox couples of Fe^{2+}/Fe^{3+} and Mn^{3+}/Mn^{4+}. It was shown that the cation-doping of LiMnPO$_4$ by electrochemically non-active metals seems to be more attractive than the mixed Mn-Fe compounds, because along with its electrochemical performance improvement this provides a constant voltage operation of the material based on a single redox reaction Mn^{3+}/Mn^{2+} [30]. It was shown that the most effective dopant for LiMnPO$_4$ is Mg [31].

Powder properties and the electrochemical performance of cathode material are strongly affected by the preparation technique. It also affects the cathodes cost and production rate. Conventional solid state reaction has several drawbacks. High-energy consumption due to the prolonged multi-step high temperature processes, heterogeneous composition and severe agglomerations of particles are only some of those disadvantages. As it was shown above, several techniques were adopted to prepare nanostructured $LiMnPO_4$ cathode with narrow particle size distribution. The best results were obtained for $LiMnPO_4$ prepared *via* sol-gel, hydrothermal and co-precipitation routes. However, these techniques use the very low concentration of starting materials, which leads to the very low production rate. Thus, these processes are very difficult to be used for the commercial production of cathode materials. Therefore, it is crucial to develop an easy to scale-up and cost-effective technique, which will allow producing high-performance nanostructured $LiMnPO_4$, which is chemically and morphologically homogeneous, has narrow particle size distribution (monodispersed) and requires the simplest and cheapest producing apparatuses.

3. PREPARATION OF $LiMnPO_4$ BY SPRAY PYROLYSIS AND ITS ELECTROCHEMICAL PERFORMANCE

Among other synthesis methods of cathode materials, spray pyrolysis (SP) is well-known as single step, continuous and easy scale-up technique [32, 33]. This method produces fine spherical particles with homogeneous chemical composition in a short time [34, 30]. In our systematic research on the preparation of cathode materials for lithium batteries using SP technique [32, 33, 35-37], we have shown that various lithium metal oxides and phosphates nanoparticles could be successfully prepared by SP and these nanoparticles exhibited enhanced electrochemical performance.

The details of the SP facility are described elsewhere [32, 33]. Mainly the SP facility consists of an ultrasonic nebulizer, a laminar flow aerosol reactor and an electrostatic precipitator. The sprayed droplets are carried to the reactor, heated by an electric furnace, by air and converted into solid oxide particles through the process of evaporation of a solvent, precipitation of solute, drying, pyrolysis and sintering within the laminar flow aerosol reactor. The resulting particles were collected at the reactor exit by the electrostatic precipitator at 150 °C (this temperature avoids the water condensation in the precipitator). Among the other advantages, this synthetic technique allows an easy control of the resulting powder properties and morphology. The final product consists of non-agglomerated spherical particles.

Nanostructured $LiMnPO_4$ particles could be successfully synthesized by SP at wide range of the synthesis temperatures from 400 to 800 °C [38]. The precursor solution consisted of the water solution of lithium and manganese nitrates and phosphoric acid in the stoichiometric ratio. While the sample prepared at 400 °C was amorphous, the XRD patterns of the samples obtained at the temperatures 500 °C and higher were single phase olivine structures with an orthorhombic *Pnma* space group. The crystallinity of powders increased with the SP synthesis temperature. The SP powders were spherical in shape (Fig. **2**). The as-prepared samples were dry ball-milled with carbon and heat treated at 500 °C to prepare $LiMnPO_4/C$ composites, which were tested as cathodes for lithium batteries. At a charge/discharge rate of 0.05 C, the cell exhibited first discharge capacities of 70 mAh g^{-1} at room temperature and 140 mAh g^{-1} at 55 °C.

The Mg-doped lithium manganese phosphate cathode materials of a general formulae $LiMg_xMn_{1-x}PO_4$ (x = 0, 0.02, 0.04, 0.12) were prepared by SP at 400 °C using a N_2 + 3% H_2 mixture as a carrying gas [30]. In order to increase the materials conductivity, the as-prepared samples were subjected to wet ballmilling (WBM) with acetylene black (AB) and heat-treated at 500 °C in a N_2 + 3% H_2 gas media for 4 h in a tubular furnace. The heat-treatment of as-prepared and wet ballmilled samples resulted in the formation of the single-phase orthorhombic structure with a *Pnmb* space group, which was confirmed by the XRD spectra (XRD, Rigaku, Ultima IV with D/teX Ultra, Cu Kα radiation) presented in Fig. (**3**). It was shown, that the relation between the lattice parameters and the Mg substitution level follows Vegard's Law [39], and an increase in x in $LiMg_xMn_{1-x}PO_4$ lead to a lattice parameter decrease. The carbon added during wet ballmilling allowed forming of the $LiMg_xMn_{1-x}PO_4/C$ composites with about 100 nm particles of active material connected with each other by a few nanometers thick carbon layers as it was shown by field-emission scanning electron microscopy (FE-SEM) and transmission electronic microscope (TEM) data. It was suggested that the addition of carbon during WBM could improve the electrical contact between the electrode material particles and reduce the particles agglomeration. The composite particles had a narrow particles size distribution with a mean particle size around 100 nm.

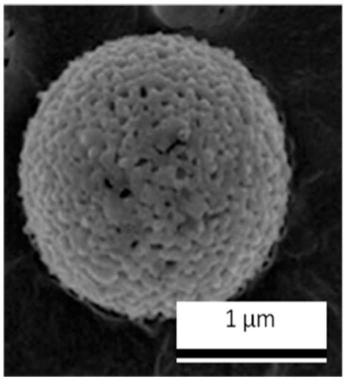

Fig. (2). SEM images of the $LiMnPO_4$ prepared by SP.

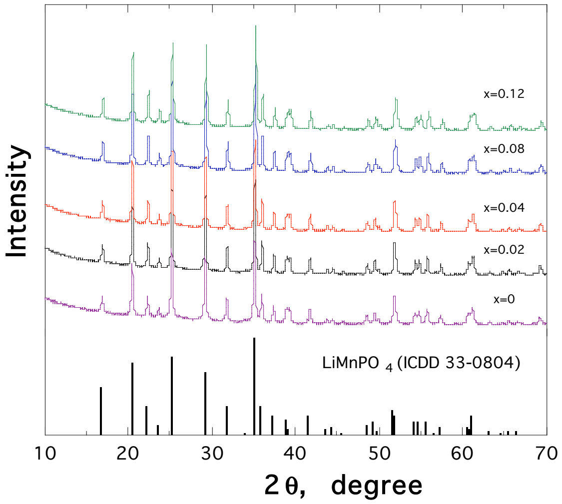

Fig. (3). XRD patterns of $LiMg_xMn_{1-x}PO_4/C$ (x = 0, 0.02, 0.04, 0.12) composites prepared by a combination of SP with WBM and heat-treated at 500°C.

The composite cathodes were successfully cycled in a lithium cell under galvanostatic conditions [30]. The highest discharge capacity of 91 mAh g^{-1} was shown by the LiMg$_{0.04}$Mn$_{0.96}$PO$_4$/C cathode when cycled to 4.4 V cutoff voltage. The charge cutoff voltage increase to 4.9 V lead to the cell capacity increase, and the LiMg$_{0.04}$Mn$_{0.96}$PO$_4$/C cathode at 0.1C charge-discharge rate exhibited a discharge capacity of 154 mAh g^{-1}, which is more than 93% of the theoretical value for this compound. The cathode materials exhibited a good rate capability under the galvanostatic charge-discharge.

In our recent work [36], the effect of various cutoff voltages on the electrochemical performance of LiMnPO$_4$ cathode was studied. The cathode material was prepared by a combination of SP with wet ballmilling. The carbon content in the final LiMnPO$_4$/C composite was 10 wt%. The composite cathode was prepared by doctor blade technique by mixing the LiMnPO$_4$/C carbon composite with PVdF binder and the additional amount of carbon, which led to the total carbon content of 20 wt% in the composite cathode. The cathode was cycled in lithium half-cell. Fig. (**4a**) shows the dependence of the cell discharge capacity on the upper cutoff voltage for this composite cathode. The discharge capacity increases with the charge cutoff voltage. The cell discharge capacity increased for about 64% when the upper cutoff voltage was expanded from 4.4 (91 mAh g^{-1}) to 4.9 V (149 mAh g^{-1}). It was suggested, that the discharge capacity increase was due to a higher level of the Li ion extraction and a longer charge stage at a higher charge cutoff voltage favored more Li ion involvement in the electrochemical process. The cell exhibited stable cycling performance under galvanostatic charge-discharge as shown in Fig. (**4b**). Fig. (**4c**) presents the discharge profiles of the cell at various discharge rates after trickle charge at 0.2 C to 4.4 V. The cell exhibited a good rate capability under these conditions, achieving about 90 mAh g^{-1} at 5 C.

Various kinds of carbon are used as a conductive agent to prepare the composite cathodes for lithium batteries. Both the abilities of the conductive carbon to conduct electrons and transport lithium ions are crucial for the electrochemical performance of the composite cathodes. From this point of view, the investigation of the effect of different conductive carbon used in the LiMnPO$_4$/C composite on its electrochemical properties is very important [40, 41]. Different carbon additives have different physical properties such as particle size, absorption ability and specific surface area. Each of these characteristics of the conductive carbon might have a significant effect on the overall conductivity of the electrode, the electrolyte absorption and, as a result, influence the overall electrochemical performance of the cell. Kuroda *et al.* [40] studied the effect of different conductive carbons such as ketjen black (KB), AB, and graphite on the electrochemical performance of LiCoO$_2$ cathode. It was shown that KB has a larger surface area and dibutyl phthalate (DBP) adsorption number, and the use of KB as a conducting agent in the composite electrode enhanced the cathode performance due to the extremely high mesoporous area and electrical conductivity of KB. Xing *et al.* [41] reported that a large mesopore specific surface area of carbon could provide favorable and quick pathways for ions to penetrate. The electrolyte adsorbed in mesoporous carbon provides intimate contact between lithium ions and the cathode material particles and improves the composite cathode conductivity [42]. Therefore, a high conductive mesoporous carbon with a larger specific surface area is a preferable choice of a conductive agent for composite cathode for the LIBs application.

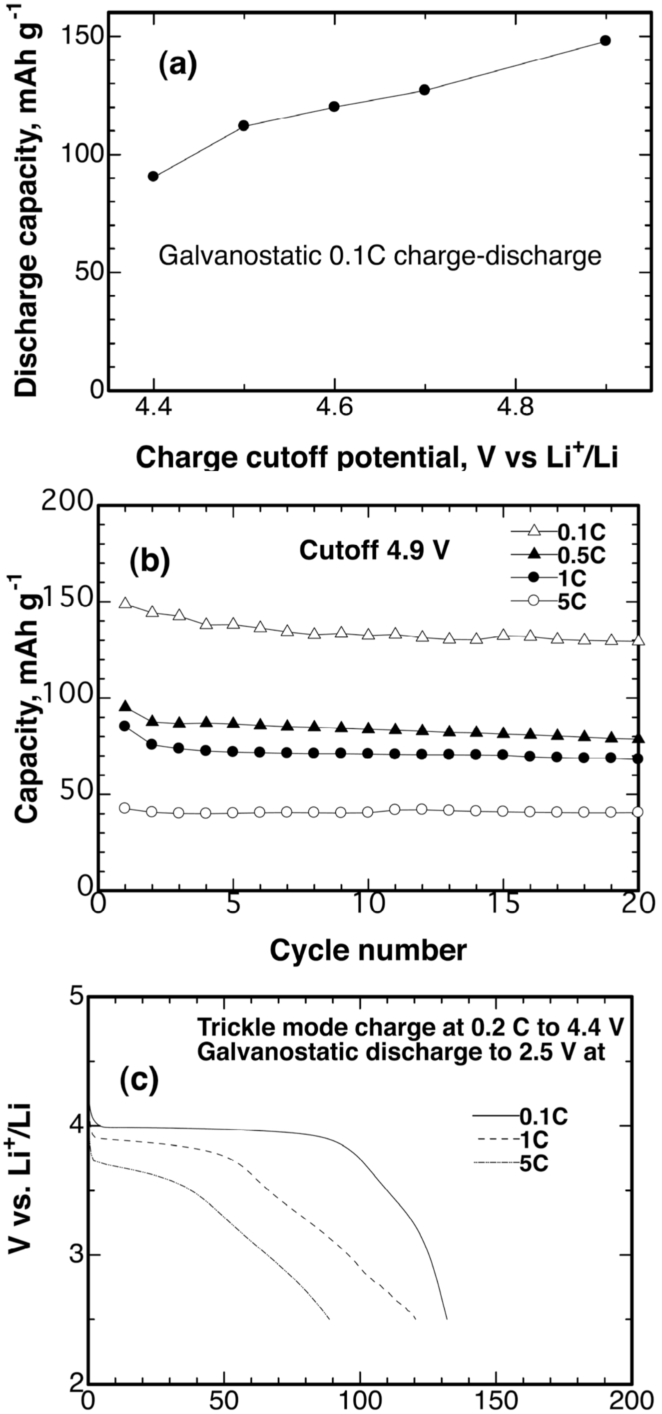

Fig. (4). (**a**) The dependence of the Li/1 M LiPF$_6$ in EC:DEC/LiMnPO$_4$ cell initial discharge capacity on upper cutoff voltage and (**b**) the cell cyclability under galvanostatic charge-discharge; (**c**) rate capability of the cell under trickle charge-mode.

LiMnPO$_4$/C composites using different conductive carbons (AB and 2 types of KB) were prepared by a

Table 1. Physical Properties of Conductive Carbon Powders Used to Prepare the $LiMnPO_4/C$ Composites

Conductive Carbon	Average Primary Particle Size, nm	BET Surface Area, $m^2\ g^{-1}$	DBP Adsorption Number, $cm^3\ 100g^{-1}$
AB	35	68	175
KB-1 (EC300J)	40	800	365
KB-2 (EC600JD)	34	1400	495

combination of SP and WBM [43]. Ketjen black samples were supplied from Ketjen Black International Company, Japan. Table **1** shows some physical properties of the conductive carbon used as conductive agents to prepare $LiMnPO_4/C$ composites. The average particle size slightly decreases in the series AB - KB1 - KB2. The specific surface area and DBP absorption number drastically increase in this row, and for KB2 these characteristics are about 21 and 3 times larger, respectively, than that of AB [43]. It was shown that the electrochemical response increased in the same sequence, AB - KB1 - KB2, and the cathode with KB2 as a conducting agent exhibited the highest discharge capacity. The AC impedance spectroscopy study showed that the electrochemical performance was due to the enhanced charge transfer and lithium ion conduction in $LiMnPO_4/KB2$. It was shown that both the specific surface area of the composite cathodes and the DBP absorption number of the conductive carbons might favor the improvement of the electrochemical performance of the cell by increasing the electronic and ionic conductivity of the cathode. Therefore, the $LiMnPO_4/C$ composite cathodes with KB2 have a high ability to absorb the electrolyte and provide easy penetration and quick Li-ion transport into the electrode structure. This cathode exhibited the highest discharge capacity of 166 mAh g^{-1} when the cell was charged to 4.9 V. This is about 97 % of the theoretical value for $LiMnPO_4$.

Further investigations of the SP preparation of cathode materials are necessary to optimize the synthesis temperature, which will decrease the energy consumption of the cathode materials production. In our recent work, $LiMnPO_4/C$ nanocomposites were successfully prepared by a combination of spray pyrolysis and wet ball-milling followed by heat treatment in the range of spray pyrolysis temperatures from 200 to 500 °C [44]. The $LiMnPO_4/C$ nanocomposite samples were used as cathode active materials for lithium batteries, and the electrochemical tests were carried out for the Li|1M $LiPF_6$ in EC:DMC = 1:1|$LiMnPO_4/C$ cell at various charge-discharge rates. It was shown that the $LiMnPO_4/C$ sample synthesized by SP at 300 °C had the narrowest particle size distribution with $\sigma_g = 1.27$ and the smallest geometric mean diameter $d_{g,p} = 72$ nm. This sample had the largest specific surface area, the smallest primary particle size and a homogeneous distribution of carbon, which resulted in the best electrochemical performance due to. At galvanostatic charge-discharge at 0.05 C, the cell delivered the first discharge capacity of 165 mAh g^{-1}, which is about 97% of the theoretical capacity of this material. Moreover, the cells showed fair good cyclability over 100 cycles.

We developed the synthesis technique, a combination of spray pyrolysis with ballmilling to prepare cathode materials for lithium batteries. The high-energy ball milling is combined with SP to insure an ultimate homogeneity of carbon mixture and compaction and better adhesion of carbon with the $LiMnPO_4$ particles. We believe that a good mechanical contact of the conductive carbon with the cathode active particles and its homogeneous distribution play a critical role in the $LiMnPO_4/C$ composite cathode performance.

The preparation technique based on a combination of spray pyrolysis with ballmilling is now employed by other research groups for the nanostructured particles preparation including $LiMnPO_4$ cathode materials. $LiMnPO_4/C$ composite was prepared by Oh *et al.* [45] and the effect of calcinations temperature on the microstructure and electrochemical performance of C-$LiMnPO_4$ was investigated. The cathode prepared at 650 °C by SP exhibited the highest capacity of 118 mAh g^{-1}. The same technique was used to prepare $LiMnPO_4$ at 400 °C in the most recent work of the same group [46]. The as-prepared $LiMnPO_4$ was heat treated at 500 °C in air then mixed with various amount of AB, which followed by heat treatment in for 1 h in an Ar gas flow. The composite cathode with about 32 wt.% of carbon exhibited the initial discharge capacity of 158 mAh g^{-1} at 0.05 C under the trickle mode charge-discharge tests.

CONCLUSION

The development of the high performance, low cost and environmentally friendly portable power sources is crucial for the zero-emission transportation and energy back-up technologies. Among the other possible candidates to replace the current commercial Co-based cathodes, which are expensive and toxic, the $LiMnPO_4$ olivine is one of the most promising materials. A brief literature survey has shown that there are tremendous efforts to develop a high-performance $LiMnPO_4$ cathode for lithium batteries. The remarkable progress has been achieved in this work, and several preparation techniques were used for the preparation of this cathode material. A combination of spray pyrolysis with ballmilling is a versatile technique to prepare a $LiMnPO_4/C$ nanocomposite cathode with narrow particle size distribution and chemical and physical homogeneity, and improved strong C-to-$LiMnPO_4$ adhesion. Therefore, $LiMnPO_4/C$ cathode prepared by this technique has the best performance reported to date. The preparation technique advantages allowed achieving up to 97 % of the theoretical capacity for this material.

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