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Electrochemical performances of $LiNi_{1-x}Mn_xPO_4$ (x = 0.05–0.2) olivine cathode materials for high voltage rechargeable lithium ion batteries

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ABSTRACT

This study demonstrated to synthesis of carbon-free lithium nickel phosphate ($LiNiPO_4$) and its analogue of manganese doped $LiNi_{1-x}Mn_xPO_4$ (x = 0.05–0.2) cathode materials by a facile polyol method and their suitability for use in high voltage lithium ion batteries (LIBs). The physicochemical properties were analyzed using X-ray diffraction, Fourier transform infra-red, Raman, field emission scanning electron microscopy (FE-SEM), energy dispersive analysis by X-ray (EDX), and electrochemical studies. FE-SEM showed that the spherical shape particles were uniformly distributed on the surface and EDX confirmed the presence of all the elements in the $LiNi_{1-x}Mn_xPO_4$ nanostructure. Substitution of Mn dopants with $LiNiPO_4$ significantly improved the electrical and electrochemical performances for $LiNi_{1-x}Mn_xPO_4$ (x = 0.05–0.2) cathodes. The highly conducting $LiNi_{1-x}Mn_xPO_4$ (x = 0.1) cathode exhibited initial discharge capacity of 94.2 mA h g^{-1} at *C*/4 rate, and 62% capacity retention after 100 cycles between 2.8 and 5.6 V. These features promote $LiNi_{1-x}Mn_xPO_4$ as a suitable cathode material for high voltage LIBs.

1. Introduction

Olivine structured $LiMPO_4$ (M = Ni, Co and etc.) phosphate cathode materials are gaining a great deal of attention recently due to their high safety, capacity, and structural and thermal stabilities for practical energy storage devices including lithium ion batteries (LIBs) and supercapacitor and photonic materials etc. [1–8]. Thereby, extensive researches have been focused towards the direction of enhancement of the energy density of practical LIBs by finding substitutes to the state of the art active and inactive materials [9–11]. Thus, the scientific community's attention has been focused on high voltage cathodes, charged to electrode potentials beyond 4.2–4.3 V vs. Li/Li^+ [9,12]. In particular, $LiFePO_4$ cathodes, an olivine phosphate material, have been widely studied and optimized for energy storage systems due to its low capital cost, eco-friendly nature, high safety, and good cyclability [13,14]. However its low energy density and low operating potential (3.45 V vs Li/Li^+) restricts its applications to small volume and powerful compact LIB devices [15,16]. To overcome these shortcomings, and develop better LIB cathodes, researchers have focused on a series of other cost-effective abundant transition metals as dopants, such as Ni, Mn, and Co in the $LiMPO_4$ (M = Ni, Mn, and Co) structure, which has been shown to produce high voltage plateaus (5.1, 4.1, and 4.7 V, respectively) compared to other transition rare earth elements [17–20].

The major drawback of $LiMPO_4$ olivine structure material is its low electronic and ionic conductivity, which restricts applications in LIBs [21,22]. The relatively poor electronic conductivities in $LiMPO_4$ olivine cathodes may be due to defect association effects, which have significant influence on migration properties of cathode materials [23,24]. Intensive studies and numerous efforts have been made to overcome this drawback for high voltage $LiMPO_4$ materials, including reducing particle size from micro to nano-size, lattice doping, carbon coating, modified chemical routes and etc. [25–31]. Nanometer sized particles deliver better electrical prop-

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erties with subsequent improved LIB performance due to its high surface area and inherent reduction of diffusion lengths for lithium ions [32,33].

Recent research works have elaborately investigated the alternatives for commercial available cathode materials ($LiFePO_4$ and $LiCoO_2$), which are still the main cathode material in the lithium ion market [34–36]. Despite their advantages and commercial availability, relatively little work has been done on Ni based olivine phosphates cathodes since basic material features are not fully understood [37,38]. Therefore, it is important to identify the major issues with regard to the synthesis of $LiNiPO_4$ as a cathode and their electrochemical and cycling performances for LIBs.

Electrical properties of $LiNiPO_4$ and their composite nanostructures have been compared previously [26,39–41], and electrical conductivity of carbon coated $LiNiPO_4$ showed 2–3 orders higher than that of bare $LiNiPO_4$ [41]. Polyol synthesized nanostructured $LiMnPO_4$ has been shown to have improved electronic conductivity and electrochemical performance [42]. Electrical conductivity of $LiNiPO_4$synthesized by the Pechini type polymer precursor method has also been reported previously [43], and their conductivity was increasing with 10% doping of Cu^{2+}, Mg^{2+}, Zn^{2+}, and Al^{3+} [44,45]. The specific capacity was also improved by $LiNi_{1-y}Mg_yPO_4$ doped graphite carbon foam $LiNi_{1-y}Mg_yPO_4$ composites [46]. Electrical conductivity of $LiNiPO_4$ was increased by doping with Zn^{2+} using the polyol method [47,48]. Ornek et al have reported the superior electrochemical and cycling performances for $LiNiPO_4$ which synthesized by solvo-thermal assisted method [12,20,49].

In this article, we have made an attempt to prepare pure and a series of Mn doped carbon-free $LiNiPO_4$ cathodes using the polyol technique, and studied the effects of Mn doping percentage on structural, electrical, electrochemical, and cycling properties of $LiNi_{1-x}Mn_xPO_4$ ($x = 0.05–0.2$) cathode materials. The $LiNi_{1-x}Mn_xPO_4$ cathode materials exhibited smaller polarization curve and improved ionic and electrical conductivities. Charge-discharge capacity was also studied.

2. Experimental

2.1. Polyol synthesis of $LiNi_{1-x}Mn_xPO_4$ particles

The Mn doped $LiNiPO_4$ samples, i.e., $LiNi_{1-x}Mn_xPO_4$ ($x = 0.05$, 0.10, 0.15, 0.20) were prepared by a facile polyol method that yielded the desired product at lower reaction temperature. Lithium acetate ($CH_3COOLi{\cdot}2H_2O$, Himedia, 99.9% Purity), nickel acetate ($CH_3COONi{\cdot}4H_2O$, Himedia, 99.9% Purity), ortho phosphoric acid (H_3PO_4, Merck), manganese acetate ($C_4H_6MnO_4{\cdot}4H_2O$, Himedia, 99.9% Purity) were used as the source materials. The polyol medium included 1, 2-propane-diol and ethylene glycol. All precursor materials were dried under vacuum at 70 °C for approximately 12 h prior to use.

Fig. 1 shows the polyol synthesis of $LiNi_{1-x}Mn_xPO_4$. The stoichiometric amount of precursor materials (acetate salts of Ni, Mn, and Li) were stirred separately in the polyol medium at ambient temperature. Then, the three precursor solutions and ortho phosphoric acid were transferred into a round bottom flask equipped with condenser unit. The resultant solution was subjected to a condensation reaction at 240 °C. The light greenish yellow precipitate was separated by continuous centrifugation and washed thrice with acetone to remove remaining organic residues. Then dried under vacuum at 150 °C for 15 h to remove physically adsorbed water. Finally, $LiNi_{1-x}Mn_xPO_4$ nanoparticles

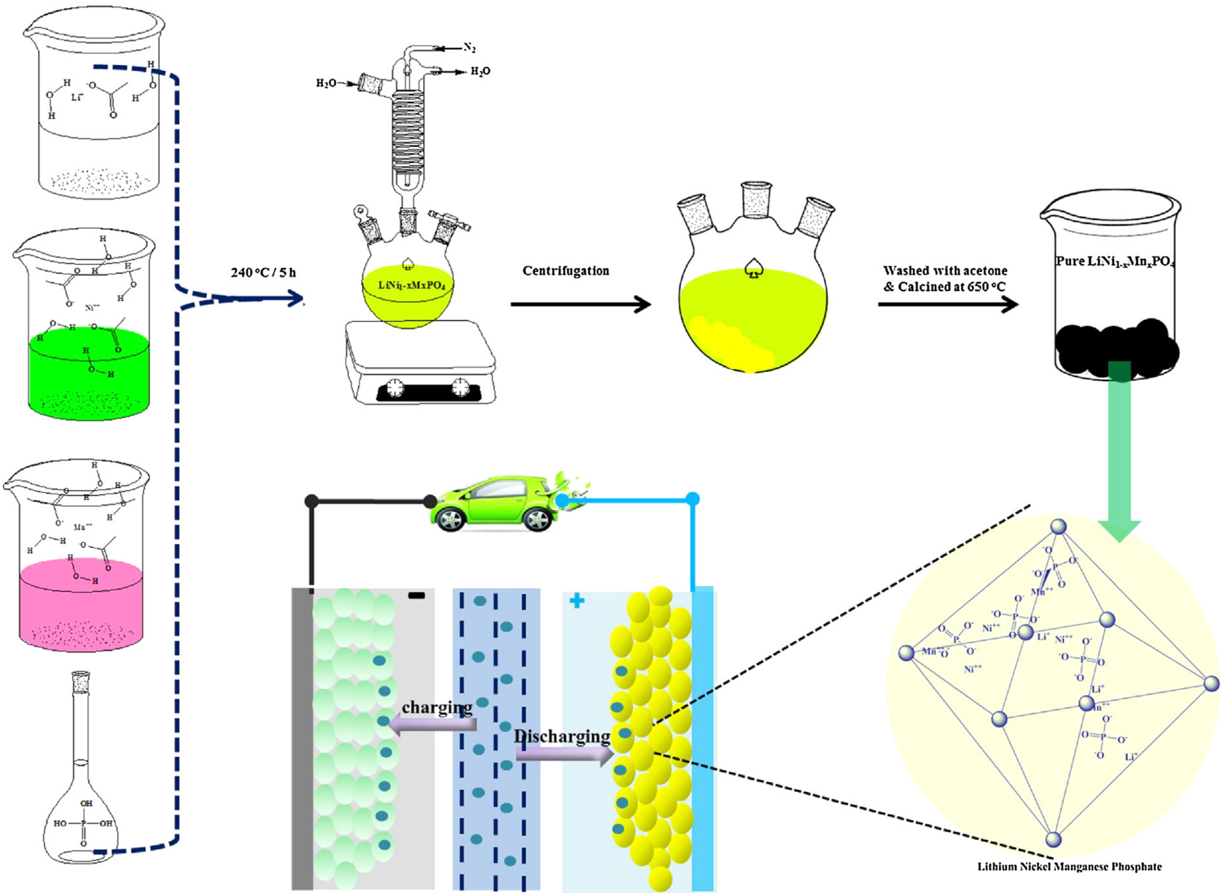

Fig. 1. Polyol synthesis of $LiNi_{1-x}Mn_xPO_4$ cathode materials.

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