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Influence of gradual cobalt substitution on lithium nickel phosphate nano-scale composites for high voltage applications

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ABSTRACT

The carbon-free LiNiPO₄ and cobalt doped LiNi_{1 - xCo_xPO₄/C (x = 0.0-1.0) were synthesized and investigated for} high voltage applications (>4 V) for Li-ion batteries. Nano-scale composites were prepared by handy sol-gel approach using citric acid under slightly reductive gas atmosphere (Ar-H₂, 85:15%). Structural and morphological characteristics of the powders were revealed by X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM) and inductively coupled plasma (ICP). Except for a small impurity phase (Ni_3P), phase pure samples crystallized in the olivine-lattice structure with a linear relationship between lattice parameters (a, b and c) and chemical composition. The FE-SEM images proved that LiNiPO₄/C particles (50–80 nm) did not agglomerate, and showed that as the cobalt content was higher agglomeration had increased. The electrochemical properties of all electrodes were investigated by galvanostatic charge-discharge measurements. Substitution of Ni²⁺ by Co²⁺ caused higher electronic conductivities and showed more effective Li^+ ion mobility. When the cobalt content is 100%, the capacity reached to a higher level (146.2 mA h g^{-1}) and good capacity retention of 85.1% at the end of the 60 cycles was observed. The cycling voltammogram (CV) revealed that LiCoPO₄/C electrode improved the electrochemical properties. The Ni $^{3+}$ -Ni 2 redox couple was not observed for carbon free LiNiPO₄. Nevertheless, it was observed that carbon coated LiNiPO₄ sample exhibits a significant oxidation (5.26 V)-reduction (5.08 V) peaks. With this study, characteristics of the $LiNi_1 - {}_xCo_xPO_4/C$ series were deeply evaluated and discussed.

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1. Introduction

Lithium orthophosphates $LiMPO_4$ (M = Fe, Co, Ni, Mn) with the olivine-type structures are captivated considerable attention as intercalation electrode materials for rechargeable Li-ion batteries due to their high capacity, high voltage, environmental friendly, cost effectiveness. stable even at over charge and preferable thermal stability during charge-discharge processes [1-3]. Major problems like the optimization of synthesis procedure and the low electrical conductivity were resolved within the last one and half decade for LiFePO₄, which is a promising material for secondary Li-ion batteries with a continuous rising requirement of the global consumption. In particular, LiFePO₄ shows acceptable redox reversibility, fast Li⁺ ion mobility, lower costs and high energy density (170 mA h g^{-1}) comparable to that of conventional LiCoO₂ cathode material [4,5]. However, the primary disadvantage of the lower voltage (~3.45 V vs. Li) is not being able to provide the requirements for today's mobile applications [6]. This factor can be overcome by selective doping with Ni, Mn and Co, which can produce high voltage

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plateaus as 5.1 V, 4.1 V and 4.7 V, respectively [7–9]. At this point, Co or Ni based LiMPO₄ electrode materials come forward as promising materials on the pathway to future superior batteries [10]. The electrochemical properties of LiCoPO₄ are currently under intensive investigation for several parameters to improve the discharge capacity and capability. whereas LiNiPO₄ fundamental dynamics are not vet brightened. Although LiNiPO₄ exhibits 5.1 V potential for battery applications, production of LiNiPO₄ is one of the handicaps that is not easy to overcome. Primarily, it has the poor electronic conductivity which is several orders of magnitudes lower than for LiFePO₄ or LiCoPO₄ [9]. Thus, this material has ever exhibited an admissible kind of electrochemical activity only when heavily carbon coated [11,12]. Secondly, the synthesis procedures of LiNiPO₄ have not been optimized yet. Mostly the solid state syntheses have been used in published studies [3,12,13]. This type of hightemperature routes lead to another problem; the formation of side phases and various impurities [13]. This leads to the third obstacle concerning the production of large particle size. It is well-known that the synthesis techniques play a crucial role in nano-scale particle production, and is related to the improvement in terms of physical as well as electrochemical properties of produced electrode materials for rechargeable batteries [14,15]. Another problem is the low electrolyte stability at high voltage ranges [16].







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2. The contribution of this work in the literature

The purpose of this paper is to synthesize pure LiNiPO₄ and $LiNi_{1-x}Co_{x}PO_{4}/C$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) compounds and to analyze the effects of cobalt substitution on the electrochemical performance of LiNiPO₄/C. All nano- and micro-composites were produced by sol-gel process, which is an uncomplicated, well-known and effective method. Thus, the method ensures the possibilities of (1) production of particles in nano-scale, (2) formation of conductive carbon coating and (3) synthesis of gradual cobalt doping to investigate the structural, morphological and electrochemical properties of LiNiPO₄. The combination of these three approaches for the in-situ synthesis of LiNiPO₄ has been rarely reported. In addition, the electrochemical characteristics of LiNiPO₄ in the literature are not comprehensive. Table 1 summarizes that the comparison of our study with some of the published articles, which is about nickel and/or cobalt based olivine phosphate materials. The structural, morphological and electrochemical properties of the synthesized materials are carefully investigated and discussed. Achieved brilliant results and comments based on it are presented to the reader in the subsequent sections.

3. Materials and methods

3.1. Sample preparation and conditions

Pure LiNiPO₄ and Co doped LiNi_{1 - x}Co_xPO₄/C (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) materials were synthesized by sol-gel synthesis. Nickel (II) nitrate (Merck \geq 99%), diammonium phosphate (Merck \geq 99%) and lithium nitrate (Sigma-Aldrich \geq 99%) were dissolved in purified water with a molar ratio of 1:1:1. Then, added the stoichiometric amount of cobalt (II) nitrate (Merck \geq 99%). Aqueous solution rigorously stirred at 40 °C for 24 h and obtained slurry precursor was heat treated in a tube furnace at 650 °C for 8 h under reductive annealing atmosphere (Ar-H₂ 85:15%) for the carbon free material. The carbon coated LiNiPO₄ particles and Co doped LiNi_{1 - x}Co_xPO₄/C composites were used same starting compounds (except Co source), which interacted in distilled water and a proper amount of citric acid monohydrate (Fluka \geq 99%) was added

Table 1

The comparison of our study to the published studies of some of the $LiNiPO_4$ or $Li(Ni-Co)PO_4$ -C articles (the background color in red indicates similarities and green color indicates non-similarities with our work).

Electrode	Synthesis method	Carbon source	Doping element(s)	Reference
LiNiPO ₄	Sol-gel synthesis	-	_	Our Study
LiNiPO ₄ -C	Sol-gel synthesis	Tannic acid	-	Our Study
LiCoPO4-C	Sol-gel synthesis	Tannic acid	Co (0.2, 0.4, 0.6, 0.8, 1.0 mol)	Our Study
LiNiPO ₄	Solid-state	-	_	[17]
LiNiPO ₄	CAM sol-gel method	-	-	[18]
LiNiPO ₄	Non-aqueous sol-gel	-	Co (0.25, 0.33, 0.66, 1.0 mol)	[16]
LiNiPO ₄	Pechini method	-	-	[19]
LiNiPO ₄	Solution combustion technique	-	Cu and Mg (0.1, 0.2, 0.3, 0.4, 0.5 mol)	[20]
LiNiPO ₄	Pechini method	-	Eu (0.01 mol)	[21]
LiNiPO ₄	Solid-state	-	57Fe (0.01 mol)	[22]
LiNiPO ₄	Polyol method	-	-	[23]
LiNiPO ₄	Solid-state	-	-	[12]
LiNiPO ₄	Solid-state	-	Mg (0.5 mol)	[24]
LiNiPO ₄ -C	Solvothermal & solid- state	Sucrose	-	[25]
LiNiPO ₄ -C	Pechini & sol-gel	Graphitic carbon foams	-	[11]
LiCoPO4-C	Hydrothermal	Not available	-	[26]
LiCoPO4-C	Pechini & sol-gel	Carbon nanofiber	-	[27]
LiCoPO ₄ -C	Sol-gel	Sucrose	-	[28]
LiCoPO ₄ -C	Solvothermal	Oleylamine	-	[29]

References mentioned in the table: [11,12,16-29].

as a chelating compound. Citric acid is widely used as a chelating agent due to its carboxylic groups [19,30,31]. During gelation, it provides strong bonding with metal ion through its carboxylic groups leading to a homogeneous precursor gel with finer particle size [32]. Then, this composition was stirred slowly until a liquid formed and the solution was heated at 40 °C for 24 h with constant agitation to form fully homogeneous appearance. Secondly, the gel was heated at 350 °C for 3 h to remove water and decomposition of nitrate in air atmosphere. Thirdly, the produced powder was ground and 10% (weight) tannic acid was added into the obtained powder as a reducing material and noble carbon source. Finally, the resulting slurry was heated in a tube furnace at 650 °C for 8 h (heating and cooling ramp ≈ 0.5 °C min⁻¹) under flowing of Ar-H₂ 85:15% gas. As a result of this procedure, all obtained powder from the derivative LiNiPO₄ olivine structure.

3.2. Characterization

The crystallographic structure of the samples was recorded by an X-ray diffractometer on a RIGAKU D-max 2200 with Cu/K α ($\lambda = 0.154$ nm). The diffracted intensities were recorded in the 2θ range 15°–65°. The cell parameters and cell volumes were calculated with the program Unit-Cell [33]. A HITACHI SU8010 field-emission scanning electron microscopy and JEOL JEM 2100-F high resolution transmission electron microscopy were used to observe particle sizes and morphological properties of the materials. The carbon ingredients of the synthesized materials were determined using inductively coupled plasma analysis by PERKIN OPTIMA 2000DV.

The electrodes were made by mixing 88% active material, 6% polyvinylidenefluoride (PVDF) as binder and 6% acetylene black as conductive additive in N-methylpyrolidinone (NMP) followed by coating the slurry onto aluminium foil as current collector. And then the slurry form was dried at 80 °C for 12 h. The prepared electrodes were generated by pressing under 200 MPa pressure for provide fixed thickness. The electrodes were dried at 100 °C under vacuum for 24 h. The electrolyte was a solution 1 mol L^{-1} LiPF₆ in ethylene carbonate and dimethyl carbonate with the equal volumes. Lithium foil was used as the anode and counter electrodes. The separator was selected 2300 microporous polypropylene membrane. The assembly of the 2032 coin-type cell was carried out in a nitrogen glove box (MBraun-Labstar). The produced cells were galvanostatically charged-discharged at 24 °C between 2.6 and 5.6 V vs. Li⁺/Li under a constant current density of 0.1 C, 0.5 C, 2 C and 5 C on the potentiostat device (BASi Epsilon), $1 \text{ C} = 167 \text{ mA h g}^{-1}$ [9]. The cyclic voltammetry was recorded between 3.2 and 5.6 V with a scanning rate of 0.05 mV s^{-1} . The electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an ac voltage of 0.05 mV s⁻¹ over the frequency range from 0.1 Hz to 10 kHz. The electrical conductivity measurements were conducted with a four probe conductivity measurement system.

4. Results and discussions

4.1. Effects of Co^{2+} doping on the structure

XRD spectra of the pure LiNiPO₄ and Co doped LiNi₁ – $_x$ Co_xPO₄/C (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) nanocomposite materials are shown in Fig. 1. It can be seen that all the patterns display well resolved diffraction peaks, which can be indexed to olivine structure and these sharp peaks in the patterns specify that the powders are in high degree of crystallinity. The miller indices (h–k–l) of all the peaks correspond to a single phase (except the very low-level peaks of Ni₃P) in *Pnma* space groups. Additionally, no diffraction peak related to carbon is determined in the XRD patterns, which are due to the low degree of crystallinity of the residual carbon or the very low carbon content to be detected. Pure LiNiPO₄ and carbon coated LiNiPO₄/C samples have not included any impurity phase. The reason for that may be either presence of carbon derived

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