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Study on Vanadium Substitution to Iron in $Li_2FeP_2O_7$ as Cathode Material for Lithium-ion Batteries

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ABSTRACT

A series of $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0$, 0.025, 0.05, 0.075, and 0.1) cathode materials for LIBs were prepared by the sol-gel method. Structural characterization of $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0$, 0.025, 0.05, 0.075, and 0.1) samples was conducted by synchrotron X-ray diffraction. The morphology and oxidation states of Fe^{2+} and V^{3+} in the $Li_2Fe_{1-3x/2}V_xP_2O_7$ samples were confirmed by scanning electron microscopy and magnetic susceptibility measurements, respectively. The electrochemical measurements indicated that $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0.025$) delivered the higher reversible capacity of 79.9 mAh g^{-1} at 1 C in the voltage range of 2.0 - 4.5 V with higher 77.9% capacity retention after 300 cycles than those of $Li_2FeP_2O_7$ (48.9 mAh g^{-1} and 72.6%). Moreover, the rate capability of $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0.025$) were also significantly enhanced through vanadium substitution to iron of $Li_2Fe_{1-3x/2}V_xP_2O_7$. The vanadium substituted to Fe2 site of $Li_2FeP_2O_7$ decreases Li occupying the Li5 position in the FeO_5 unit, leading to a low degree exchange between Li and Fe in the MO_5 (M = Li and Fe). The low degree cation disorder was beneficial to lithium-ion extraction/insertion during the charge-discharge process and hence enhances the capacity and rate capability.

1. Introduction

$LiMPO_4$ (M = Fe, Co, Ni, Mn, and combinations thereof)) compounds have been considered to be among the most promising cathode materials for lithium-ion batteries intended for applications in electric vehicles (EVs) or renewable energy systems, due to their excellent electrochemical performance, low cost, and environmental friendliness. $LiMPO_4$ (M = Fe, Co, Ni, Mn, and combinations thereof)) compounds have stable three-dimensional (3D) frameworks containing PO_4 polyanions with strong covalent bonds, as well as M^{2+}/M^{3+} redox couples at high voltage (> 3.4 V), and thus offer high energy densities, long cycle life, excellent thermal stability, and high operating safety [1–4]. Recently, the pyrophosphates $Li_2MP_2O_7$ (M = Fe, Mn, and Co), which contain P_2O_7 polyanions formed by two PO_4 units sharing one O-O edge, have also been identified as cathode materials for lithium-ion batteries [5–18]. $Li_2FeP_2O_7$ prepared by conventional solid-state synthesis at 600 °C delivered a reversible specific capacity of around 110 mAh g^{-1} with an operating voltage of about 3.5 V at 0.05 C in the voltage range of 2.0 - 4.5 V [6]. Compared to its couterpart $LiFePO_4$ (~ 166 mAh g^{-1}), $Li_2FeP_2O_7$ has a lower theoretical capacity (~ 110 mAh g^{-1}) because of the relatively heavy weight of the pyrophosphate and the extraction of only one electron per formula unit. However, $Li_2FeP_2O_7$ showed a slightly higher operating voltage (~ 3.5 V vs. ~ 3.4 V) and lower synthesis temperature than $LiFePO_4$. Not only for these advantages, but also due to the possibilities of extracting two electrons from $Li_2MP_2O_7$ (*e.g.*, M = Mn) with a theoretical capacity of ~ 220 mAh g^{-1}, the pyrophosphates $Li_2MP_2O_7$ (M = Fe, Co, Ni, Mn, and combinations thereof)) have already received more attention as promising high voltage cathode materials for lithium-ion batteries [5–18].

So far, $Li_2FeP_2O_7$ as cathode for LIBs suffers from the low rate capability or poor cycling stability because of its low electronic and ionic conductivity [5–18]. As the counterpart of $Li_2FeP_2O_7$, $LiFePO_4$ also showed the low electronic and ionic conductivity [3,6,7]. However, over the past decades, simple and effective techniques, including carbon coating, morphology control, particle size reduction, and aliovalent doping, have been made to overcome this obstacle to the application of $LiFePO_4$ [1–4]. Among these techniques, aliovalent doping was intensively investigated as one of most effective techniques to improve the electrochemical performance of $LiFePO_4$, as the electronic and ionic conductivity of

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$LiFePO_4$ was critically increased by several orders of magnitude through a small amount of aliovalent doping [19,20]. Among the many aliovalent elements, active vanadium element was widely employed as a dopant in $LiFePO_4$ because of its various oxidation states ($2^+, 3^+, 4^+, 5^+$) [21–36]. Despite the enhanced electrochemical performance through vanadium doping, there is still no agreement on the explanation. The reasons given for the improvement in the electrochemical performance vary from replacement of Fe, Li, or P by vanadium so as to enlarge lithium or electron pathways [24,25,28–30], to no vanadium substitution entering into the $LiFePO_4$ host structure [26], or formation of an impurity phase V_2O_3 coating [27].

To date, there is no report on aliovalent doping in $Li_2MP_2O_7$ (M = Fe, Co, Ni, Mn, and combinations thereof)) compounds. Therefore, a study of aliovalent doping in $Li_2MP_2O_7$ could provide new insights to understand the mechanism behind the effects of aliovalent doping on the electrochemical performance of pyrophosphates. Here, we prepared a series of V-incorporated $Li_2FeP_2O_7$ samples by the sol-gel method, assisted by citric acid and sucrose as the carbon sources and reductive agent. The detailed structures, magnetic properties, and electrochemical performance of V-incorporated $Li_2FeP_2O_7$ were investigated. We found that $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0.025$) delivered the higher reversible capacity of 79.2 mAh g^{-1} at 1 C in the voltage range of 2.0 - 4.5 V with higher 75.8% capacity retention after 300 cycles than those $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0$) (49 mAh g^{-1} and 65.8%, respectively). The improved electrochemical performance for $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0.025$) can be attributed to vanadium substitution into its Fe sites by synchrotron X-ray diffraction (SXRD). The vanadium substituted on Fe2 sites of $Li_2FeP_2O_7$ is beneficial to decrease Li occupying the Li5 position in the FeO_5 unit, leading to a low degree exchange between Li and Fe in the MO_5 (M = Li and Fe). The low degree cation disorder could facilitate lithium ion extraction/insertion, and hence enhance the capacity and rate capability.

2. Experimental

2.1. Material synthesis

The $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0$, 0.025, 0.05, 0.075, and 0.1) compounds were prepared by the citric acid (CA) assisted sol-gel method from the starting materials LiH_2PO_4, $(CH_3COO)_2Fe$, NH_4VO_3, and sucrose. The molar ratio of Li/Fe/V/P/sucrose was 2: (1 - 3x/2): x: 2: 0.34 ($x = 0$, 0.025, 0.05, 0.075, and 0.1). The starting materials were dissolved in distilled water, and then citric acid was added to this solution under stirring (molar ratio of CA/sucrose = 1.5: 1). Each solution was heated gently with continuous stirring to remove the excess water at 80 °C in a thermostatic water bath to obtain a viscous gel, which was then dried in a vacuum oven at 80 °C to yield a xerogel. The xerogels were then ground, heated to 600 °C at a heating rate of 5 °C min^{-1} in a tube furnace, and then kept at that temperature for 10 h under flowing high purity Argon atmosphere, followed by natural cooling to room temperature.

2.2. Materials characterization

The phase identification of the $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0$, 0.025, 0.05, 0.075, and 0.1) compounds was carried out by synchrotron X-ray diffraction (SXRD, Melbourne, Australian Synchrotron). The SXRD data were collected over a 2θ range of 3 - 80° with a step size of 0.0038°, using a wavelength of 0.825 Å. The morphology and particle size of the $Li_2Fe_{1-3x/2}V_xP_2O_7$ sample were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), using JSM-7500FA and JEOL JEM-2011 instruments, respectively. The specific surface area was measured by the 15 point N_2 absorption Brunauer-Emmett-Teller (BET) method using a Quanta Chrome Nova 1000. The carbon content of the $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0$, 0.025, 0.05, 0.075, and 0.1) was characterized by thermogravimetric analysis (TGA, Mettler Toledo) in air over the temperature range of 50 - 800 °C with a ramp rate of 10 °C min^{-1}. The carbon content was also verified by Vario EL (Elementar, Germany) CHNS Elemental Analyzer. The magnetic measurements were carried out using a 14 T physical properties measurement system (PPMS), equipped with a vibrating sample magnetometer (VSM), over a wide temperature range from 2 to 340 K in a 100 Oe magnetic field. The electronic conductivity measurement of $Li_2Fe_{1-3x/2}V_xP_2O_7$ ($x = 0$, 0.025, 0.05, 0.075, and 0.1) powders was adopted with a Jandel RM3 four-point probe measurement system at room temperature. The specimens used for electronic conductivity measurement were disk-shaped pellets with 8 mm in diameter and 1.5 mm in thickness.

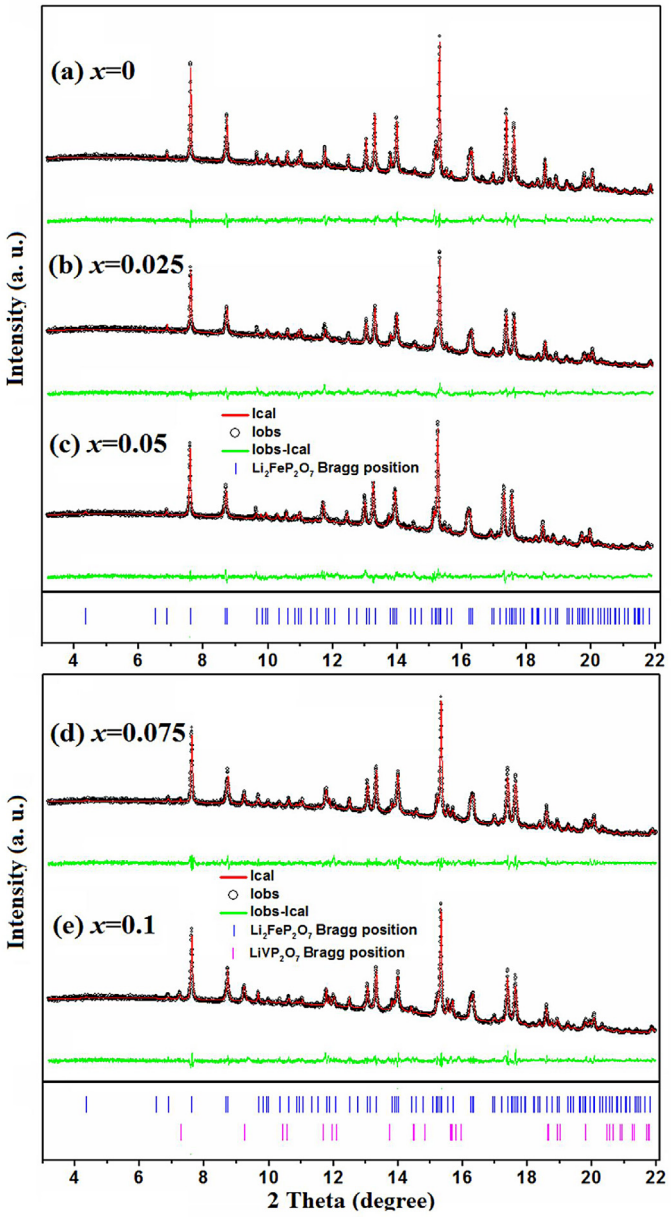

Fig. 1. Synchrotron X-ray diffraction (SXRD) patterns for $Li_2Fe_{1-3x/2}V_xP_2O_7$ (a) $x = 0$, (b) $x = 0.025$, (c) $x = 0.05$, (d) $x = 0.075$ and (e) $x = 0.1$.