

V-insertion in Li(Fe,Mn)FePO₄T. Wu^a, J. Liu^a, L. Sun^a, L. Cong^a, H. Xie^{a,*}, A. Abdel-Ghany^b, A. Mauger^c, C.M. Julien^c^a Northeast Normal University, National and Local United Engineering, Laboratory for Power Batteries, 5268 Renmin Str., Changchun, PR China^b Inorganic Chemistry Department, National Research Centre, Behoes Street, Dokki, Giza, Egypt^c Sorbonne Université, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), CNRS UMR 7590, 4 place Jussieu, 75005 Paris, France

HIGHLIGHTS

- 3 mol.% vanadium is inserted in LiMn_{0.8}Fe_{0.2}PO₄.
- V³⁺ substitutes for Fe²⁺.
- Electrochemical properties are improved over 500 cycles at 0.1C rate.
- V³⁺/V²⁺ is observed at 1.8 V.
- Diffusion coefficient of Li⁺ is multiplied by a factor 2.

ARTICLE INFO

Keywords:

Olivine
Vanadium doping
Cathode materials
Lithium-ion batteries

ABSTRACT

Insertion of 3% vanadium in LiMn_{1-y}Fe_yPO₄ has been investigated, with $y = 0.2$ corresponding to the highest manganese concentration before the stress/strain field degrades the electrochemical performance. V substitutes for Fe²⁺ in the trivalent state V³⁺. This substitution is accompanied with the formation of Fe vacancies while Mn remains in the Mn²⁺ valence state, leading to a composition LiMn_{0.8}Fe_{0.2-0.045}V_{0.03}□_{0.015}PO₄ where □ is a Fe vacancy. The comparison between electrochemical properties of a pristine sample and a sample with 3 mol.% vanadium made of particles with the same morphology (spherical particles with the same dispersion 100–150 nm in size) and same carbon coating (same conductivity of the carbon layer) is reported. Although the vanadium is in the V³⁺ state at open circuit voltage (2.6 V) before cycling, a reversible V³⁺/V²⁺ is observed when the potential of the half-cell is lowered below the redox potential of 1.8 V vs Li⁺/Li, due to Li-vacancies. The V-insertion improves the electrochemical properties, due to a synergetic effect of an increase of the lithium diffusion coefficient by a factor two and an increase of the electric conductivity at any Li-concentration during the cycling process, in contradiction with prior claims that attributed the increase of conductivity to V-based impurities.

1. Introduction

Padhi et al. proposed LiFePO₄ as a candidate for Li-ion batteries in 1997 [1]. After the carbon coating has been found to solve the problem of poor electrical conductivity [2], and after the removal of impurities [3], the use of this material has grown exponentially to commercialize safe and fast-charging Li-ion batteries with long shelf life for power applications [4]. Outstanding rate capabilities have been reached with C-Li₄Ti₅O₁₂ as the counter-electrode [5], demonstrating that two-phase reactions during the charge-discharge process are not power-limiting, contrary to some prior claims [6]. Actually, the performance of the LiFePO₄-based Li-ion batteries is limited only by the theoretical capacity of LiFePO₄ (170 mAh g⁻¹) and the low capability of the graphite

chosen in commercial batteries to avoid the penalty of energy density implied by the lower operational voltage with the Li₄Ti₅O₁₂ anode. In addition, LiFePO₄ is thermally stable and environmentally benign.

Despite the remarkable performance of pure LiFePO₄ after carbon-coating, many attempts have been made to dope it in order to increase the electrical conductivity. Indeed, the carbon coating reduces the conductivity of the powder since the electrons that reach the surface of a particle can be driven to the current collector through the percolating conductive carbon coat. However, the coat has no effect on the conductivity inside the particle. To minimize the way to go for an electron to reach the surface, the size of the particle has been reduced to typically 100 nm or less. However, this reduction in size also increases the effective surface area of the solid-electrolyte interface (SEI), which is

* Corresponding author.

E-mail address: xiehm136@nenu.edu.cn (H. Xie).

resistive, and it also increases the cost of manufacturing. These considerations were the motivation for the attempts of doping that have been reviewed for instance in [7], despite the fact that doping is not energetically favorable and that the unbreakable PO_4^{3-} bonding prevents charge balance by oxygen-vacancy formation [8–10]. Moreover, in case the aliovalent ion goes on the Li-site, a case met for instance with Al [11], the whole one-dimensional motion of all the Li-ions in the corresponding channel is blocked, so that the doping is actually deteriorating the electrochemical properties [9,12].

There is, however, a case of particular interest that is vanadium insertion in LiFePO_4 . There is a consensus to claim that the introduction of vanadium increases the electrical conductivity [13–22], but the reasons are controversial. In principle, a variation of the unit cell of the lattice with the concentration of vanadium should be an evidence of the introduction of this element into the matrix. A decrease of the unit cell volume suggested a substitution of V for P [16] before these authors revised their position; they said that it was impossible and claimed that it is due to a substitution of V for Fe with V in the V^{3+} valence state, with a charge compensation due to Fe vacancies to form $\text{LiFe}_{1-3y/2}\text{V}_y\text{PO}_4$ up to a limit of solubility of 10 mol.% vanadium [18]. In the same way, a linear decrease of the cell volume upon substitution up to 4 mol.% [17] and 7 mol.% [20] was attributed to the substitution of V for Fe. In contrast, we can also find in the literature an increase of the cell volumes with 3 mol.% substitution [15], irregular cell volume changes with 5 mol.% substitution [19], and even no cell volume change upon adding up to 10 mol.% vanadium [23], in which case the enhanced electrochemical performance was attributed to the formation of the conductive V_2O_3 impurity phase.

This last result is also the conclusion of other works claiming that the vanadium does not penetrate in the LiFePO_4 crystal lattice, not even at the 1% substitution level, based on both experimental results and simulation [24]. The formation of V_2O_3 was also mentioned by Aleees [25]. Other impurities have also been invoked. Zhang et al. [19] observed $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ impurities at any doping level, and reported that the electronic conductivity of the V-doped samples is higher than that of LiFePO_4 when the vanadium content is less than 7 at. % because $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ impurities could enhance the electronic conductivity of LiFePO_4 [26,27]. Then the fact that the electronic conductivity of the V-doped samples is higher than that of LiFePO_4 when the vanadium content is less than 7 at. % was attributed in [19] to the fact that $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ impurities enhance the electronic conductivity of LiFePO_4 . On another hand, the electronic conductivity of the V-doped samples gradually decreases with the vanadium concentration. The reason invoked was that the carbon content decreased with the increase of the vanadium content, because the pyrolytic carbon was increasingly consumed for the reduction of V^{5+} to V^{3+} during the synthesis process, and the electronic conductivity of the samples depends mainly on the residual carbon content rather than the vanadium content. The excessive carbon would be a barrier for the diffusion of Li^+ ions during the charge/discharge process, and the inactive carbon would reduce the ratio of the active material, leading to a decrease in capacity. Finally, Zhang et al. [19] concluded that the enhancement of the electrochemical performance should be mainly due to the existence of a small amount of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ rather than the doping of V in the host lattice.

To our knowledge, no study has been made of the V-doping of $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$ even though the undoped $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$ solid solution has been the subject of tremendous efforts since a decade, since the introduction of manganese in this solid solution increases the voltage, and thus the energy density (see [28] for a review). One purpose of this work is to study V-doping of $\text{LiMn}_{1-y}\text{Fe}_y\text{PO}_4$. However, the Mn concentration must not exceed $1-y = 0.8$, otherwise the local Jahn-Teller distortions introduced by Mn^{3+} inside the material are too large, and the electrochemical properties are decreased [29]. For this reason, this concentration was chosen in this study. The vanadium concentration was reduced to 0.03 to be significantly lower than the limit of solubility reported in the literature, and avoid the formation of V-based

impurities that have been reported as poisoning the powder. This 3% doped material will be named V-LMFP in the following, while the undoped $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ sample will be named LMFP.

For LiFePO_4 , we consider that the best choice of the temperature for the carbon coating is 650 °C [30]. However, the carbon coating of LMFP is more difficult than that of LiFePO_4 , because the affinity between Fe and C has been lost with the manganese. Consequently, the conductivity of the carbon deposited onto LMFP is smaller than that of the carbon deposited at the same temperature on LiFePO_4 . Therefore, it is desirable to increase the temperature of the deposition to recover a more conductive carbon. We have thus chosen the temperature of 700 °C, which is the highest temperature that can be used before the heating generates impurities [31].

2. Experimental

2.1. Synthesis

The V-LMFP sample was prepared by a two-step solid phase method. The stoichiometric amounts of Li_2CO_3 (99.9% Shanghai China Lithium Industrial Co. Ltd.), MnCO_3 (Analytical reagent (AR) Sinopharm Chemical Reagent Co. Ltd.), FePO_4 (AR Sinopharm Chemical Reagent Co. Ltd.), NH_4VO_3 (AR Sinopharm Chemical Reagent Co. Ltd.), $\text{NH}_4\text{H}_2\text{PO}_4$ (99.0% Tianjin Guangfu Technology Development Co. Ltd.) and Super P were mixed in deionized water and ball-mill for 20 h. Then the mixed slurry was dried at 55 °C in the oven. After drying, the mixture was calcined in the N_2 atmosphere at 350 °C for 20 h. Subsequently, the precursor powder was mixed with glucose in deionized water and ball-milled for 24 h, then the slurry was dried at 55 °C, followed by calcination at 350 °C for 4 h and 700 °C for 10 h in N_2 atmosphere to coat the particles with carbon. The pure material was prepared by the above methods without the vanadium doped.

2.2. Characterization

The crystalline phase of the as-prepared materials was identified by powder X-ray diffraction (XRD) patterns recorded on the Rigaku-Dmax2500 diffractometer with Cu-K α radiation ($\lambda = 154.06$ pm). The 2θ -angle varied from 10 to 90° at a scanning rate of 0.05° min^{-1} . The Raman spectra were recorded on a LabRAM HR Evolution-HORIBA Raman system at room temperature, with an excitation laser wavelength (λ_e) of 488 nm. The morphology of the materials was observed by scanning electron microscopy (SEM, Hitachi S-5500). The detailed particle, crystal information, and elements distribution of as-prepared samples were analyzed by high resolution transmission electronic microscopy (HRTEM, JEOL-2100F) coupled with an energy dispersive X-ray spectroscopy (EDS). A superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMSXL-5) was used to measure the dc magnetic susceptibility (χ_m) of the samples in the temperature range 4.2–300 K. The XANES experiments were performed at the Canadian Light Source (CLS) located at the University of Saskatchewan. The Mn and V K-edge XANES were obtained at the Soft X-ray Microcharacterization Beamline (SXRMB).

2.3. Electrochemical measurements

The cathodes were prepared by the active material (V-LMFP), conductive agent (Super P), and binder (poly (vinylidene difluoride)) (PVDF) in a weight ratio of 80:10:10, mixed with N-Methyl-2-pyrrolidone (NMP) to make a slurry. This slurry was then cast onto the aluminum foil with a diameter of 1.3 cm. All the half-cells were coin-type cells assembled in an Ar-filled glove box (Mbraun, PRS380/S11-0736) using a Li foil negative electrode (China Energy Lithium Co, Ltd), and a standard electrolyte solution 1 mol L^{-1} $\text{LiPF}_6/\text{EC}/\text{DMC}$ (1:1 by volume). The charge and discharge tests were performed on a LAND system (CTA2001A, Wuhan Land Electronic Co. Ltd.) with a potential

Download English Version:

<https://daneshyari.com/en/article/7725371>

Download Persian Version:

<https://daneshyari.com/article/7725371>

[Daneshyari.com](https://daneshyari.com)