

**Experiment title:**

Vanadium structural role in doped LiFePO_4 : XAS and XRD determination of V oxidation state and location in the olivine lattice.

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A set of XAS spectra at the Fe, Zn, Ni and V K-edge has been successfully collected for a wide group of synthetic LiFePO_4 powders doped with V, Ni and Zn. Also few V-doped cathodes have been measured at both the V and Fe K-edge. The analysis of the Pre-edge peaks of Fe and V allowed to quantitatively determine the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox ratio, and the V oxidation state (3+). The data have been used –along with structural determination by laboratory source X-ray Diffraction data – to characterize the studied samples.

V-DOPED SAMPLES

The samples have been shown to contain V in the olivine lattice, and not as secondary phases. The substitution mechanism $\text{Li}_{1-x}\text{Fe}_{1-x}\text{V}_x\text{PO}_4$ has thus been confirmed by both XRD data and theoretical XANES calculations which agree well with experimental XANES data at the V K-edge. V K-edge EXAFS data are currently under examination.

The fact that V is in the 3+ state in both the oxidised and reduced electrodes means that it does not participate in the redox reaction (Li exchange upon Fe reduction/oxidation) in the voltage range used for the electrode cycling.

Comparison of the Fe redox ratio with the electrochemical data determined for the cathodes allowed to ascertain that the Fe utilization increases with the V content despite V is not electroactive.

The higher Fe utilization is tentatively explained by the presence of Li vacancies in the M1 site produced by the proposed substitution mechanism. Moreover, also local lattice distortion triggered by the V entry in the M2 site could help Li exchange.

The results of this study have been published in Moretti et al., (2013) Journal of the electrochemical society (160 (6), A940-A949).

Ni-DOPED SAMPLES

Also these samples have been shown to contain Ni in the olivine lattice, and not as secondary phases. The substitution mechanism $\text{Li}_1\text{Fe}_{1-x}\text{Ni}_x\text{PO}_4$ has thus been confirmed by both XRD data and XANES data on the Ni oxidation state. These data are preliminary, and further data have been later collected at ELETTRA. The local structure measured by XAS shows that average Fe-O and Ni-O distances do not change appreciably with Ni doping indicating that the reduction of cell size is mainly associated with the presence of shorter Ni-O distances at M2 sites.

The study of Fe and Ni K-edge data allowed to publish a paper by Tabassam et al. (2012), Journal of Power Sources, 213, 287-295

Zn-DOPED SAMPLES

Also these samples have been shown to contain Zn in the olivine lattice, and not as secondary phases. The substitution mechanism $\text{Li}_1\text{Fe}_{1-x}\text{Zn}_x\text{PO}_4$ has thus been confirmed. These data are still under study. In particular, EXAFS data will be compared with XRD data to determine the geometrical variations induced by the Zn entry in the M2 site.

Further theoretical XANES calculations will be performed by the MXAN code in order to reproduce the spectral features found in the experimental data at the Zn K-edge, while theoretical EXAFS calculations is being performed by GNXAS package. A further paper will be submitted on the Zn-bearing LiFePO_4 samples.



Structural and Electrochemical Characterization of Vanadium-Doped LiFePO₄ Cathodes for Lithium-Ion Batteries

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A series of Li_{1-x}Fe_{1-x}V_xPO₄/C (with 0 ≤ x ≤ 0.1) samples have been synthesized using a wet chemistry method and characterized via Rietveld structure refinement of powder X-ray diffraction data. The amount of impurities is negligible up to x = 0.07, whereas for higher V content also Li₃V₂(PO₄)₃ phase is formed in minor quantities. The unit cell parameters of the olivine phase undergo anisotropic variations that cause an overall decrease of the unit cell volume with increasing Vanadium content. Structural data suggest that V enters the olivine lattice substituting for Fe. Compared with those of pure LiFePO₄, V doped compounds have higher specific capacities especially at high rates delivering about 100 mAhg⁻¹ at 10C rate. Local geometry and oxidation state of Fe and V in cycled electrodes was determined by X-ray absorption spectroscopy at the Fe and V K-edge. The data demonstrate that V is trivalent in both the oxidized and reduced electrodes meaning that V does not participate to the redox process. However, with increasing the vanadium content in the LiFePO₄ lattice, the amount of Fe that reversibly oxidizes and reduces during battery cycling increases with an enhancement of the electrochemical performances.

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Driven by the consumer market, more efficient use of renewable energy sources and by possible applications in electric vehicles, the demand for advanced energy storage batteries has increased significantly during the past decade. Because of their characteristics, lithium ion batteries are one of the most important candidates for all the above applications. At present the main challenges for development of lithium ion batteries for mass market are cost, safety, energy and power densities, charge/discharge rate and service life.^{1,2}

In this context, the olivine LiFePO₄ is considered a possible alternative to commonly used metal oxides (LiMO₂) and spinels (LiM₂O₄) positive electrodes in Li-ion batteries, because of its reasonably high theoretical energy storage capacity (170 mAhg⁻¹) combined with electrochemical and thermal stability, low cost and environmental benignity.³⁻⁵ The main limitations of LiFePO₄ are its low intrinsic electronic conductivity (10⁻⁹ Scm⁻¹), which prevents full use of its theoretical capacity and the low Li-ion diffusion coefficient (ranging between 10⁻¹¹ and 10⁻¹³ cm²s⁻¹).^{6,7} Several approaches have been proposed and explored to overcome these drawbacks, including particles coating with carbon^{8,9} or other conductive species,^{10,11} and decreasing particles size to nano-scale.^{12,13}

In recent years, lattice engineering has also been investigated as a possible way to obtain electronically conductive phospho-olivine.^{14,15} Although many publications report the feasibility of aliovalent doping (e.g. Mo⁶⁺, Ti⁴⁺, Al³⁺, Zr⁴⁺) and its beneficial role on the electrochemical properties of LiFePO₄,¹⁶⁻²⁰ this issue is still under debate due to conflicting results.²¹⁻²³ Some authors observed that the improved electronic conductivity after metal doping may arise from carbon contamination²⁴ or phosphides formation.²⁵ Moreover, using atomistic simulation techniques, Islam et al.²⁶ found that only divalent metal dopants can be introduced in the LiFePO₄ lattice while aliovalent doping is not tolerated.

Among the different transition metals employed as dopants, vanadium is one of the most intriguing elements because of its various oxidation states and different coordination chemistry. Furthermore, vanadium can form electrochemically active compounds such as Li₃V₂(PO₄)₃,²⁷⁻²⁹ α,β-LiVOPO₄^{30,31} and V_xO_y³²⁻³⁴ that can find application as cathode materials in lithium ion batteries. Recent studies on V-doped LiFePO₄ have shown that vanadium substitution into olivine lattice enhances the electrochemical performances of this cathode material.³⁵⁻⁴⁶ However, there are still open issues about coordination geometry and oxidation state of the dopant that prevent a precise

correlation between structure and the improved electrochemical performances.

Yang³⁶ and Sun³⁸ observed V³⁺ substitution on Fe site and consequent increase of the unit cell parameters. On the contrary, Ma⁴⁰ showed an inverse dependence between unit cell volume and the amount of V⁴⁺ replacing the iron up to 7 at% of substitution. After that limit, secondary phases as VO₂ and Li₃V₂(PO₄)₃ are formed. Zhang⁴¹ limited the range of solid solution between V and Fe up to 3 at.% substitution before the formation of Li₃V₂(PO₄)₃ and LiVOPO₄. Zhao⁴⁷ investigated, by X-ray absorption spectroscopy, the solubility of V at both Fe and P sites showing the formation of Li₃V₂(PO₄)₃ and the absence of any structural changes of the LiFePO₄ phase. As also pointed out in the recent work of Hong⁴⁶ these discrepancies could probably arise from the different synthesis methods used.

In this context, and with the aim of clarifying whether aliovalent doping of LiFePO₄ is possible or not, we synthesized a series of V-doped LiFePO₄ samples and systematically studied the effect of V-doping on the crystal lattice parameters using a variety of techniques. Among many possible substitution mechanisms (such as those reported e.g. in Meethong et al.¹⁵), we decided to study the effect of V³⁺ substitution for Fe²⁺ trying to balance this aliovalent substitution by creating a lithium vacancy in the M1 site according to the formula Li_{1-x}Fe_{1-x}V_xPO₄. The study of different substitution mechanisms other than those reported in the literature can be useful in view of the fact that different V oxidation states and different defect creation mechanisms can lead to different electrochemical properties.

The samples have been characterized by X-Ray Diffraction (XRD) and X-Ray Absorption Spectroscopy (XAS) techniques to provide detailed information on structural variation as a function of the V content, oxidation state of the dopant and its location in the lattice. The electrochemical performances of doped samples have been evaluated in comparison with those of pristine LiFePO₄.

Experimental

Synthesis.— The Li_{1-x}Fe_{1-x}V_xPO₄/C (with 0 ≤ x ≤ 0.1) series was synthesized using as starting materials LiNO₃ (Sigma-Aldrich, purity >99%), Fe(NO₃)₃·9H₂O (Sigma-Aldrich, purity >98%), NH₄H₂PO₄ (Sigma-Aldrich, purity >99%), NH₄VO₃ (Sigma-Aldrich, purity >99%) and D(+)-Glucose (Sigma-Aldrich, ACS Reagent) as carbon source. The molar ratio between phosphorus and carbon was fixed to 1:4, while molar ratio between metals was changed accordingly with the target stoichiometry. The precursors were dissolved in water and heated under constant stirring at 60°C. The resulting solid precursor

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journal homepage: www.elsevier.com/locate/jpowsourStructural study of LiFePO_4 – LiNiPO_4 solid solutionsLubna Tabassam^a, Gabriele Giuli^a, Arianna Moretti^a, Francesco Nobili^a, Roberto Marassi^a, Marco Minicucci^{a,b}, Roberto Gunnella^{a,b}, Luca Olivi^c, Andrea Di Cicco^{a,b,d,*}^a School of Science and Technology, University of Camerino, I-62032 Camerino, Italy^b CNISM, Consorzio Interuniversitario di Struttura della Materia, Sezione di Fisica, Università di Camerino, Italy^c Synchrotron ELETTRA, Strada Statale 14, I-34149 Basovizza, Trieste, Italy^d IMPMC, Université Paris 6, CNRS, Campus Jussieu, F-75005 Paris, France

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ABSTRACT

Modifications of the local structure and lattice parameters in $\text{LiFe}_{1-x}\text{Ni}_x\text{PO}_4$ ($0 < x < 0.15, 0.9, 1.0$) olivine-type solid solutions have been studied by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Samples have been synthesized and characterized in our laboratory, and a preliminary electrochemical characterization shows that Ni doping increases slightly the performances in Li-ion cells at low Ni concentrations x . Results of both XRD and XAS techniques are consistent and indicate ordering of Li in the M1 site, and of Fe and Ni in the M2 site of the olivine structure. Ni doping is found to induce an anisotropic shrinking of the unit cell with both Fe and Ni six-coordinated with oxygens, occupying distorted octahedral sites. The local structure measured by XAS shows that average Fe–O and Ni–O distances do not change appreciably with Ni doping indicating that the reduction of cell size is mainly associated with the presence of shorter Ni–O distances at M2 sites. Possible connections among the presence of a distribution of distorted octahedra of different size in the structure and different electrochemical performances of the material as a function of doping are briefly discussed.

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1. Introduction

In recent times, considerable efforts have been devoted to study physical and chemical properties of Li-phosphate olivines, mainly for their possible use as a storage cathode for rechargeable lithium batteries. Compounds under consideration include LiMPO_4 olivines where M is a transition metal (see for example [1]). Key factors for using these materials in batteries are their electrical and ion (Li^+) conductivities.

In particular, the olivine-type LiFePO_4 (triphylite) has attracted much attention as a suitable cathode material for high-power Li-based batteries [2]. LiFePO_4 has been extensively studied because of its attractive properties such as inexpensiveness, non-toxicity, high theoretical capacity ($\sim 170 \text{ mAh g}^{-1}$), excellent cycling and thermal stability [3–5].

The key drawbacks of LiFePO_4 are its low electronic conductivity and reversible capacity. Various synthesis and processing

approaches have been employed to improve the conductivity and cyclability of the LiFePO_4 [6–8]. Many studies have been devoted to optimize the material for better electrochemical performance and try to understand the lithium intercalation/deintercalation mechanism [9–11].

It has been shown [1,2] that significant increases of the electrical conductivity can be induced by controlled nonstoichiometry and cation doping, improving the performances of current electrodes.

Structural changes in triphylite due to solid solutions of a metal M with iron ($\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$) may have significant effects on its solid electrolyte properties, including rates of Li diffusion and activation energies. Thus, detailed knowledge of structure in solid solutions is important in the development and design of Li-based olivine storage cathodes. Several structural studies have been performed on $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ solid solutions [12–18], few discussing structural variations that occur as a function of M content x . In particular, no detailed structural works on $\text{LiFe}_{1-x}\text{Ni}_x\text{PO}_4$ solid solutions have been attempted so far, although this material can be possibly useful in a wide range of concentrations in view of the similarity of the cation radii.

In this work, we present new results of a structural study of $\text{LiFe}_{1-x}\text{Ni}_x\text{PO}_4$ solid solutions for different Ni concentration x .

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