



Iron and lithium-iron alkyl phosphates as nanostructured material for rechargeable batteries



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ABSTRACT

Inorganic/organic hybrid materials composed by iron atoms bonded to an alkyl phosphate can be easily synthesized by mixing at 110 °C iron chlorides with tri-alkyl phosphates.

Since structural information on these products are lacking and taking into account that lithium/iron organic hybrid materials are important in lithium ion battery technology we report here the physico-chemical characterization of different hybrid lithium/iron butylphosphates. These materials are characterized by the presence of elongated hexagonal crystals stable up to 315 °C. The insertion of lithium does not affect the local structure. Thanks to such structures the material can be electrochemically-cycled and Li ions can find facilitated pathways for travel and redox reactions.

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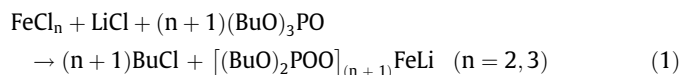
1. Introduction

Synthesis of lithium iron alkyl phosphates can be carried out by easy procedures and using cheap starting reactants. In particular, by mixing appropriate amounts of an alkyl phosphate with lithium and iron chlorides at temperatures in the range 100–120 °C the formation of a solid product occurs. Even if similar reactions have been reported elsewhere, information on the structural features of the products are lacking [1]. As these hybrid materials are potentially of utmost importance in developing lithium ion battery technology [2–4], detailed knowledge on their structure is of basic interest to set up new low-cost materials for lithium ion batteries.

Here we report physico-chemical information on the products obtained by mixing at 110 °C tri *n*-butyl phosphate with iron chloride. We will also show that lithium insertion in these compounds gives interesting nanostructured materials worth to be tailored for the realization of lithium ion batteries.

2. Experimental part

Reagent grade tri *n*-butyl phosphate (TBP), FeCl₃, FeCl₂, LiCl from Sigma Aldrich were used as received. Fe-TBP samples were prepared by adding TBP to weighted amount of FeCl₃ or FeCl₂ in order to achieve the desired Fe-to-TBP molar ratio *R* (*R* = 0.018, 0.16 and 0.33). Lithium containing samples were prepared by adding the Fe-TBP solution (*R* = 0.16) to a weighted amounts of lithium chloride to obtain a 1:1 Li/Fe molar ratio and maintaining stirring at 110 °C for at least 48 h. The solid product of the reaction



was filtered and washed three times with *n*-octane. Hereafter, the corresponding products will be indicated as TBP/Fe(III), TBP/Fe(III)/Li, TBP/Fe(II), and TBP/Fe(II)/Li.

TGA–DSC measurements have been performed in a TGA-DSC 1 Star System by METTLER TOLEDO with a 10 min^{−1} heating rate in N₂ or air (30 ml min^{−1}) after treatment in nitrogen at 100 °C for 30 min to eliminate physisorbed molecules.

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FT-IR spectra were acquired by a Shimadzu Prestige 21 FTIR spectrophotometer equipped with a Specac Golden Gate Attenuated Total Reflectance (ATR) accessory, whose advantages are reported in Supporting Information (Fig. S1).

SEM/EDS were carried out by a Cambridge 360 SEM equipped with a LaB₆ filament and with an energy dispersive X-ray spectrometer (EDS) INCA 250 (acceleration voltage 20 kV, working distance 25 mm).

XRD measurements were carried out with a Bruker D5000 vertical goniometer equipped with Cu anode (K α radiation $\lambda = 1.5418$ Å), using a 0.03° step size per point in 2 θ mode.

Electrochemical tests were performed by a VMP Multichannel Potentiostat (Perkin Elmer Instruments) at room temperature, using a T cell. The positive electrode was obtained by mixing the sample with carbon super S and Teflon as binder. For the negative and reference electrodes, metallic lithium was used. The separator was glass wool and a LiPF₆ solution in dimethyl carbonate and diethyl carbonate (molar ratio 1:1).

Due to the Fe(II) tendency to be oxidized Fe(II)-containing samples were prepared under inert (nitrogen) gas.

3. Results and discussion

3.1. IR spectra

Fig. 1 compares the ATR-IR spectra of the synthesized products (with and without Li) at R = 0.16, chosen as representative, with that of pure TBP.

Band attributions are reported in the same figure [5]. In TBP/Fe(III) and TBP/Fe(II) the P = O band typical of pure TBP at 1271 cm⁻¹ is absent while new bands appear at 1160, 1101 and 1062 cm⁻¹ suggesting that the P = O groups are interacting with Fe(III) and Fe(II), in accordance with previous observations [6]. Further bands (at 563, 514, 467, 413 cm⁻¹ attributable to Fe-O vibrations) confirm the phosphate-iron interaction.

No difference among samples with different R was observed, therefore the synthesis leads always to the same final product. Moreover, no significant difference was also observed between the spectra of the samples with and without lithium, indicating that lithium is located far apart from the P = O groups and that the structure at the nano-scale is quite insensitive to the presence of lithium.

3.2. SEM/EDS

TBP/Fe(III) at R = 0.018, 0.16 and 0.33 have been analysed by SEM and a representative image (R = 0.16) is shown in Fig. 2A.

The samples are crystalline with few micrometer thick and of tens of micrometers long crystals. Their structure was found to be quite independent on the R values, as expected from FT-IR results. At a deeper sight an elongated hexagonal structure can be envisaged. This shape is expected to reflect the symmetry of the atomic structure of the unit cell beneath.

EDS gave the chemical fingerprint of these products: in accordance with the SEM and FT-IR, EDS shows that also the chemical composition is quite unaffected by the R parameter, giving O/P atomic ratio of 2.8 ± 0.3 and Fe/P atomic ratio 0.30 ± 0.02 , showing good accordance with the theoretical values derived considering reaction (1). Also, the chlorine absence in the final products is a further suggestion that reaction (1) takes place to completeness.

SEM micrographs have been also collected for TBP/Fe(III)/Li (Fig. 2B): the elongated crystals show a fibrous structure. This indicates that the insertion of lithium ion within the microstructure influences the structural arrangement at the meso-scale.

The atomic O/P ratio is 4.8 ± 0.5 and the atomic Fe/P one is 0.23 ± 0.02 showing a slight variation of the relative atomic abundance induced by the presence of the Lithium ion.

3.3. XRD

The XRD spectra of the four samples are shown in Fig. 2C. All the samples show the same pattern, but in the samples prepared from FeCl₂ the diffraction peaks are located at slightly higher angles. This highlights the lowering of interplanar distances when passing from Fe(III) to Fe(II), reasonably due to the lower number of counterions accompanying iron ion causing lower steric hindrance. Moreover, both lithium-containing samples have reflections at higher angles with respect to the corresponding lithium-free samples, revealing an electrostriction due to the lithium ions high charge density. The two factors have the same effect in reducing the lattice parameter, so the sample with Fe(II) and lithium has the lowest lattice parameter. Moreover, peaks of lithium-containing samples are generally broader, showing an increase of disorder induced by the introduction of the lithium salt, consistently to SEM results.

Since the main peak and the successive ones are in the ratio $1 : 1/\sqrt{3} : 1/2$ the crystals are characterized by a hexagonal bidimensional structure consistent with the elongated crystals shape observed by SEM. A schematic structure is therefore shown in Fig. 2D. The lattice parameter (a) is related to the interplanar distances (d) and the angle θ of the peak centres by the equations

$$2d \sin \theta = n\lambda \quad (\text{eq. 1})$$

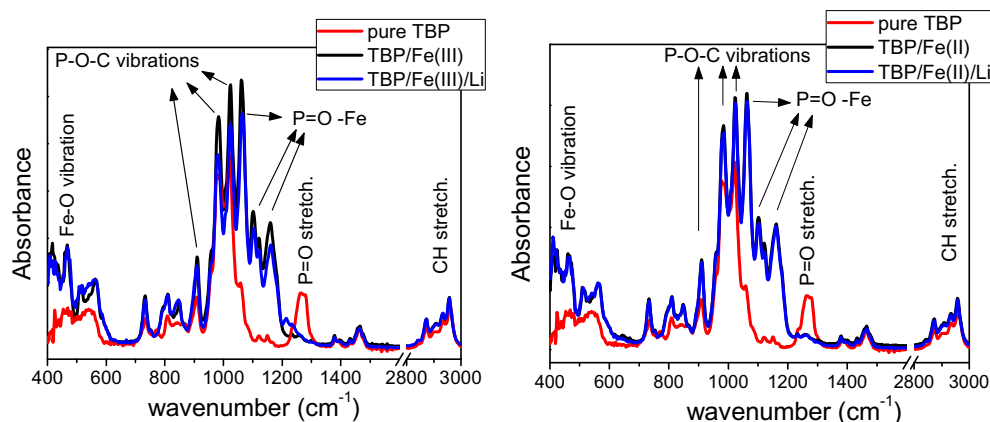


Fig. 1. ATR spectra of solid samples and pure TBP (red line). Left panel: TBP/Fe(III) (black line), TBP/Fe(III)/Li (blue line). Right panel: TBP/Fe(II) (black line), TBP/Fe(II)/Li (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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