**Toward Understanding The Lithiation/delithiation Process in
Fe_{0.5}TiOPO₄/C Electrode Material for Lithium-ion Batteries**

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Abstract

Fe_{0.5}TiOPO₄/C composite was used as anode material for LIB and exhibits excellent cycling performance when the electrode is cycled in two different voltage ranges [3.0-1.3V] and [3.0-0.02V] where different insertion mechanisms were involved. A detailed *in situ* XANES spectroscopy study coupled to the electrochemical analyses, clearly established that the structure of Fe_{0.5}TiOPO₄/C electrode materials is preserved when cycled between 3.0 and 1.3V. Furthermore, a formation of new phase at the end of first discharge was evidenced, with a reversible capacity of 100 mAhg⁻¹ after 50 cycles at C/5 rate. At highly lithiated states, [3.0-0.02V] voltage range, a reduction–decomposition reaction highlights the Li-insertion/extraction behaviors, and low phase crystallinity is observed during cycling, in addition an excellent rate behavior and a reversible capacity of 250 mAhg⁻¹ can still be maintained after 50 cycles at high cycling rate 5C.

Keywords:

Lithium-ion batteries; anode material; Fe_{0.5}TiOPO₄; Reaction mechanism; *in situ* XRD; *in situ* XANES.

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1. Introduction

Titanium-oxophosphates are among the most interesting series of materials, exhibiting wide variations in physical properties, including linear and nonlinear optical, electro-optical and structural properties, which form the basis of a large number of applications. As a result, they have been the subject of extensive experimental and theoretical investigations in the past years [1-11]. This class of materials has attracted a considerable interest as host material for lithium-ion batteries (LIB), after encouraging investigation of the electrochemical properties of LiTiOPO_4 [12] and $\text{Ni}_{0.5}\text{TiOPO}_4$ [13], in which the reversible electrochemical insertion/deinsertion was first revealed.

Many attempts have been made to investigate the electrochemical properties of $\text{M}_{0.5}\text{TiOPO}_4$ (Ni, Co, Fe, Cu, Mg...) [14-23]. The structure of $\text{M}_{0.5}\text{TiOPO}_4$ phosphates was solved by different research groups [24-30], reporting the monoclinic space group $\text{P2}_1/\text{c}$, with TiO_6 octahedra chains linked by PO_4 tetrahedra and large cavities, which allow rapid lithium ion diffusion. Although that the use of $(\text{PO}_4)^{3-}$ polyanions, in place of the smaller oxygen, reduces the specific capacity, it provides an open, flexible and highly stable 3D framework, due to the strong P-O covalent bonds, which prevents the oxygen release. These characteristic features provide outstanding safety properties under a possible abuse use of the batteries.

However, one of the key drawbacks of $\text{M}_{0.5}\text{TiOPO}_4$ electrodes is their low intrinsic electronic conductivity. The use of conductive carbon additives using various synthesis and processing approaches has been employed to overcome this problem [15-17, 20].

$\text{M}_{0.5}\text{TiOPO}_4$ attracts a considerable interest as anode material for LIB, but there are unresolved issues regarding its structural evolution and electrochemical behavior during cycling. The experimental examination is challenging due to the influence of the transition-metal elements and the preparation method on the structural and electrochemical features. The main concern in cycling $\text{M}_{0.5}\text{TiOPO}_4$ is the electrochemical reaction mechanism

involved during the first lithiation process, and the propensity of the material to undergo a typical mixed insertion-conversion mechanism.

In fact, previous X-ray diffraction (XRD) studies have shown that these materials lose crystallinity and become amorphous during lithiation [15, 17, 19, 20, 25, 31], with the detrimental loss of capacity after the first cycle. Like in the case of tridymite iron phosphate [32], the discharge reaction was expected to be similar to the conversion reaction of transition metal oxides [33-35], where the lithiation process leads to the decomposition of the oxide and the subsequent formation of metallic nanoparticles dispersed in a lithium oxide matrix. During the subsequent charge, such metal particles react with the lithium oxide matrix leading to a nanodispersed form of the initial metal oxide. In spite of this similarity, there is still no clear evidence that the observed reaction is simply a conversion reaction. In fact, phosphate polyanions are not forcedly expected to behave like oxides during lithiation/delithiation processes, which means that the electrochemical reactions of $\text{M}_{0.5}\text{TiOPO}_4$ with lithium might have their own intrinsic characteristics.

Our main objective in this work is to enhance the electrochemical performance of $\text{Fe}_{0.5}\text{TiOPO}_4$ anode material, comparing with our previous paper on this material [18], and by controlling the synthesis method, $\text{Fe}_{0.5}\text{TiOPO}_4$ powder with high purity was successfully prepared using sol-gel method. The second objective is to show the trade-off between specific capacity and structure crystallinity, and to gain new and detailed insights on the structural changes involved in the reaction of $\text{Fe}_{0.5}\text{TiOPO}_4$ with lithium.

Previous investigations [22] that examined the structure changes in $\text{Fe}_{0.5}\text{TiOPO}_4$ upon lithiation have identified a slight increase of the unit cell after the insertion of $1.2 \text{ Li}^+/\text{f.u}$ (chemical lithiation). According to this work, the Fe is substituted by Li during the lithiation and the material structure crystallinity decreases due to the extrusion of metallic iron from the structure. This result supports our previous work showing serious structural modifications

1 during the first electrochemical cycle [18]. Moreover, the recent in situ XRD study by Bleith.
2 et al. [31] doesn't give any details of the structure changes upon the electrochemical
3 lithiation. Despite these work on this material, a detailed understanding regarding the
4 structural changes still lacking. An in depth investigations are necessary to identify crystal
5 structure changes upon electrochemical cycling, and to provide an insight into the
6 understanding of the electrochemical properties of this material which help to optimize its
7 performance.
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9 For this aim, we used a combination of advanced characterization techniques, mainly *in-situ*
10 XRD and *in-situ* XANES, coupled with electrochemical analysis. In this work, the new
11 information obtained on the nature of electrochemical processes, and their associations with
12 the structural changes of $\text{Fe}_{0.5}\text{TiOPO}_4$ during the first cycle provide a more general guide to
13 understand lithiation/delithiation mechanisms in $\text{M}_{0.5}\text{TiOPO}_4$ anode materials for lithium ion-
14 batteries.
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16 2. Experimental

17 2.1. Synthesis

18 $\text{Fe}_{0.5}\text{TiOPO}_4$ polycrystalline powder was prepared by the sol-gel synthesis process.
19 Commercial Iron(II) acetate $\text{Fe}(\text{CH}_3\text{CO}_2)_2$ powder (99%, Fluka) was progressively dissolved
20 in a solution of H_3PO_4 (98%, Fluka) and TiCl_4 diluted in ethanol (98%, Prolabo) under
21 constant magnetic stirring. In order to maintain pH=0 at which the gel is formed, an adequate
22 volume of water was added. The gel was dried at 80 °C for 8 h to remove excess ethanol. The
23 obtained powder was ground in a mortar and put into an Al_2O_3 crucible, preheated at 450 °C
24 for 5 h and finally calcined at 850°C for 18 h with intermediate mechanical grinding for 30
25 min. The synthesis of the $\text{Fe}_{0.5}\text{TiOPO}_4$ powder was performed in an argon atmosphere. After
26 the synthesis, a carbon-coated $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ sample was obtained by mixing intimately
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1 Fe_{0.5}TiOPO₄ (85% wt.) and sucrose (15% wt.) in an acetone solution to ensure a
2 homogeneous mixture. The mixture was then heat-treated at 600°C for 5 h under argon.
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4 **2.2. Characterization**

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7 X-ray diffraction (XRD) measurements of carbon-coated Fe_{0.5}TiOPO₄ powder were carried
8 out with a PHILIPS X'Pert MPD diffractometer with a Cu K α_1 radiation ($\lambda = 1.54056 \text{ \AA}$)
9 equipped with a X'Celerator detector in the 2θ range between 10 and 90°. Rietveld
10 refinement was applied to analyze the obtained XRD patterns.
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17 Ti K-edge X-ray absorption near-edge (XANES) spectra were collected in transmission mode
18 at ambient temperature on beamline XAFS (Synchrotron Elettra, Trieste, Italy). The sample
19 was mounted into an *in situ* cell previously described elsewhere [36] and discharged at C/6
20 rate. About one spectrum per hour was collected during the first part of the first discharge
21 (about 1.5 inserted Li per unit formula).
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29 For operando experiments, specific electrochemical cells were designed for recording XRD
30 data in reflection mode [36] during cycling without stopping the battery. The electrochemical
31 cell was assembled in a glove box under controlled argon atmosphere. The XRD patterns
32 were recorded continuously during the first discharge and the first charge in galvanostatic
33 mode (C/10 rate). The data were collected every 1 hour, which corresponds to the reaction of
34 0.1 Li/ Fe_{0.5}TiOPO₄ for each XRD pattern.
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44 Thermogravimetric (TG) analysis was performed with a DTA/TG Stanton STA 781. The
45 scans were performed at a heating rate of 10 °C/min in the temperature range from 25 to
46 1000 °C. Raman spectroscopy was carried out at room temperature using LabRam ARAMIS
47 IR2, Horiba Jobin Yvon with a blue diode laser $\lambda = 473 \text{ nm}$ or helium neon laser $\lambda = 633 \text{ nm}$.
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53 **2.3. Electrochemical measurements**

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56 In order to prepare the working electrode, 75% wt. of active Fe_{0.5}TiOPO₄/C powder were
57 dispersed in N-methyl pyrrolidone (NMP) with 15 wt.% of carbon Super P, and 10 wt.% of
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poly-vinylidene fluoride PVDF. This mixture was ball-milled during 45 min. The formed slurry was tape-casted onto a Cu foil and dried at 80°C. Electrode discs were cut out from the copper foil, and dried again in vacuum at 80°C for 6 hrs.

Electrochemical measurements were carried out using coin cells (CR2032). The cells were assembled in an argon filled glove box, using the as-prepared electrode as the working electrode, lithium foil as the counter and reference electrode, a porous polypropylene (Celgard 2300) as the separator, and 1M LiPF₆ in a 1:1 ethylene carbonate: dimethyl carbonate (EC:DEC) solution as electrolyte. The batteries were tested on an BioLogic MPG2 potentiostat in galvanostatic mode at room temperature.

The *in situ* XRD and XANES measurements were performed on pellets obtained by mixing 90 wt % active material with 10 wt % carbon black, without PVdF binder.

3. Results and Discussion

3.1. Structural characterization

Before use in the lithium batteries, the synthesized Fe_{0.5}TiOPO₄ was characterized by powder X-ray diffraction. The XRD pattern analysed by the Rietveld method, using the Fullprof program [37], is shown in Fig. 1. All diffraction peaks for the carbon-coated Fe_{0.5}TiOPO₄ materials were indexed in the P2₁/c space group confirming the absence of crystalline impurities. The iron titanium oxyphosphate materials are indexed in the monoclinic P2₁/c crystal structure, with the unit cell parameters: $a = 7.3889(8) \text{ \AA}$, $b = 7.3874(8) \text{ \AA}$, $c = 7.4128(8) \text{ \AA}$, $\beta = 120.405(6)^\circ$, $Z = 4$, $V = 349.921 \text{ \AA}^3$. In Tables 1 and 2, we show a summary of the main structural parameters of this material including the main interatomic distances, obtained from the refinement of the X-ray diffraction data.

The Fe_{0.5}TiOPO₄ crystal structure showing the –Ti–O₁–Ti–O₁–Ti– chain along the c axis is plotted in Fig. 2. The titanium cation Ti⁴⁺ is coordinated to six oxygen anions forming distorted octahedral environment. Two oxygen with alternating short and long Ti–O₁ bond

lengths of about 1.78 Å and 2.26 Å, respectively, are placed along the c axis (see Table 2).

The other four oxygen ions forming the equatorial plane of the octahedron are situated at variable distances between 1.9 and 2.2 Å from the titanium.

The Fe^{2+} cations are located in a triangular based antiprism sharing faces with two $[\text{TiO}_6]$ octahedra. The Fe-O distances, shown in Table 2, are all quite similar, indicating only a slight distortion of the $[\text{FeO}_6]$ octahedra. The coordination of P^{5+} is the typical tetrahedral one, with P–O distances of about 1.5 Å (see Table 2) implying that the $[\text{PO}_4]$ tetrahedra are quite regular. The structure is built up of a corner-sharing framework consisting of infinite chains of $[\text{TiO}_6]$ octahedra along the c-axis which are linked by $[\text{PO}_4]$ tetrahedra, two successive $[\text{TiO}_6]$ octahedra of the same chain share the oxygen (O_1) atom which does not belong to the $[\text{PO}_4]$ tetrahedron. The crystal structure also provides three-dimensionally connected empty sites for intercalation of guest ions with various sizes, including lithium ions. 50% of the octahedral 2a sites are occupied by Fe^{2+} , whereas the octahedral 2d sites are unoccupied, $\text{Fe}_{0.5}\text{TiOPO}_4$ can thus be described as $[\text{Fe}_{1/2}\square_{1/2}]_{2a}[\square]_{2d}[\text{Ti}]_{4e}[\text{O}_5]_{4e}[\text{P}]_{4e}$.

To quantify the amount of carbon in the $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ composite materials, TGA analysis was carried out in air. The samples were heated from 25 to 1000 °C at a rate of $10^\circ\text{C}.\text{min}^{-1}$. Differently from the uncoated sample, the TGA curve of the composite sample $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ (Fig. 3) shows a steep weight loss of $\approx 6\%$ between 400 and 500 °C, which corresponds well to the expected loss due to carbon oxidation. An additional weight gain occurs in both samples starting from about 600°C. This process is probably related to the decomposition of the initial material causing the oxidation of divalent iron, as confirmed by X-ray diffraction and Mossbauer spectroscopy analysis of the powder recovered after the TGA analysis (not shown).

Raman spectra corresponding to $\text{Fe}_{0.5}\text{TiOPO}_4$ and $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ samples are shown in Fig.

4. The spectrum of the non-coated material (Fig. 4a) show a strong Raman band at $\sim 736\text{ cm}^{-1}$

which is typical of the O-Ti-O-Ti-O chains in the studied oxyphosphate [1-3]. The bands in the region of 830-1150 cm^{-1} and 350-640 cm^{-1} are attributed respectively to the bending and stretching vibrations of the PO_4^{3-} group. The bands between 50 and 350 cm^{-1} are associated to the external modes of the translational vibrations of the Ti^{4+} , Fe^{2+} and PO_4^{3-} ions. In the Raman spectrum of the $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ composite (Fig. 4b), in addition to those of $\text{Fe}_{0.5}\text{TiOPO}_4$, two new intense broad bands can be observed at 1345 and 1594 cm^{-1} corresponding to the typical D and G bands of the carbon coating.

3.2. Insertion/extraction process in $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$

The typical galvanostatic profiles for lithium insertion/extraction in $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ in the electrochemical window 3.0-0.02 V at C/10 rate are shown in Fig. 5. During lithium insertion, three main voltage-composition regions are identified, which can be attributed to several irreversible processes. The voltage profile quickly drops from about 3.2 V vs. Li^+/Li (open circuit voltage) to about 1.9 V followed by a plateau at ≈ 1.75 V (Process 1). After the reaction of about 1 Li, the voltage drops to 0.7 V vs. Li^+/Li , for a second plateau lasting for about 3 more Li (Process 2). The potential then slowly decreases towards 0 V. These processes correspond to the insertion of more than 6.8 Li^+ .

During Li extraction, a continuous voltage slope is observed, with the extraction of 4 Li^+ at 3.0 V. The difference between first discharge and first charge gives an irreversible loss of more than one third of the initial capacity. The first electrochemical cycle of the $\text{Li}/\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ differs significantly from the subsequent cycles (Fig. 6), during which the voltage varies continuously with the composition, without distinguishable plateaus. Such behavior has been observed for several conversion materials, such as transition metal oxides [35]. To identify the potential window in which irreversible lithium insertion takes place, galvanostatic cycling was carried out in the same conditions but in three different voltage ranges: 3.0-1.3 V, 3.0-0.5 V and 3.0-0.02 V vs. Li^+/Li (Fig. 7). In the first case, only about

1 Li^+ is inserted, with an irreversible capacity of 40 mAh/g during 1st charge (corresponding
2 to 0.3 Li/f.u.). In the other two cases, when the low cutoff voltage is fixed below 1.0V, very
3 large capacity loss is observed during 1st charge as mentioned in Fig. 7. Since the electrolyte
4 is thermodynamically unstable at these potentials, it is widely accepted to ascribe at least part
5 of the observed irreversible capacity in this potential region, to electrolyte decomposition and
6 the subsequent formation of a solid electrolyte interphase (SEI) film on the surface of the
7 $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ particles.
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10 In addition, the appearance of the potential step “sloped regions” after the first pseudo plateau
11 (process -I- in Fig. 5) clearly indicates that there is a different lithium insertion mechanism,
12 related to a deep reduction of Ti^{4+} to $\text{Ti}^{3+}/\text{Ti}^{2+}$ as observed for $\text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4$ [38] and
13 recently for $\text{Cu}_{0.5}\text{TiOPO}_4$ [23], and $\text{Fe}_{0.5}\text{TiOPO}_4$ [31], with the conversion reaction based on
14 the reduction of Fe^{2+} to metallic iron as proved by Mossbauer spectroscopy [18] and X-ray
15 absorption spectroscopy (XAS) [31] studies.
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18 As can be seen from Fig. 8, we found that by limiting the discharge voltage within process-I,
19 which corresponds to the insertion of up to 1 Li^+ , a reversible mechanism occurs. Indeed, an
20 initial feature at about 1.65 V characterizes the first charge process, and then a potential
21 pseudo plateau is observed from 1.8 V. During this process, 0.7 Li^+ ion are extracted, leading
22 to an irreversible capacity loss of 40 mAh/g over the first cycle. In the following cycles (Fig.
23 8), the material reacts with lithium nearly in a reversible manner, with a distinct voltage
24 pseudo-plateau near 1.7 and 2.1 V vs. Li^+/Li and the same lithium uptake (0.7 Li^+),
25 suggesting a multistep-type reaction of lithiation/delithiation.
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28 Fig. 9 shows the voltage vs. composition and specific capacity curves, for a cell discharged
29 down to 0.5 V. A slope voltage profile characterizes the 1st charge and subsequent
30 discharge/charge processes by an insertion/extraction of 2.2 Li ion/f.u. leading to a reversible
31 capacity of 290 mAh/g.
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1 It is obvious that the reaction of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ with lithium, during the first discharge,
2 shows one typical slope insertion process when the amount of inserted lithium exceed 1 Li
3 ion. Structural changes accompanying lithium insertion/extraction in $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ were
4 studied by *in situ* XRD. In this survey, the cells were cycled at C/10 rate with two different
5 cut-off potentials: 1.3 and 0.02 V. XRD patterns were recorded continuously during the first
6 discharge and the following charge. Fig. 10 presents the evolution of the XRD patterns and
7 the potential with the amount of reacted Li for the electrode material cycled in the potential
8 window [3.0-1.3V].
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10 The diffraction data show the gradual disappearance of the reflections of pristine $\text{Fe}_{0.5}\text{TiOPO}_4$
11 with increasing inserted Li. Simultaneously; the reflections of a new phase (A) gradually
12 grow, and almost completely replace those of the initial phase after the insertion of 1.0 Li^+ .
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14 The collected diffractograms were refined using Fullprof software (Le Bail refinement) [37].
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16 The diffraction pattern obtained after the insertion of 1 Li^+ ion (Fig. 11) can be indexed in a
17 new monoclinic cell with the same space group of the pristine ($\text{P2}_1/\text{c}$) but with different cell
18 parameters. The variation of the latter values with the amount of inserted Li^+ , reported in Fig.
19 12, is very small throughout the discharge. This observation is thus in line with a typical
20 biphasic reaction $\text{Fe}_{0.5}\text{TiOPO}_4 \rightarrow \text{LiFe}_{0.5}\text{TiOPO}_4$, with a significant increase of all unit cell
21 parameters and of the global cell volume. Indeed, 'a', 'b', 'c' and ' β ' undergo a slight
22 variations by +0.13 Å, +0.09 Å, +0.11 Å, and +1.4°, respectively. These variations of the cell
23 parameters are closely related to the change in the transition metal valence state.
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25 Even though these structural changes are usual for a two-phase reaction, the electrochemical
26 signature of this part of the discharge rather indicates a slow but steady decrease of the
27 potential, which is usually attributed to a solid solution domain. This apparent discrepancy
28 can be related to the possible variation of the conductivity of the reacting phases, or more
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generally to the kinetics of the phase transition pathway evolution during the growth of lithium-rich phase at the expense of the original $\text{Fe}_{0.5}\text{TiOPO}_4$ phase.

During the first charge, only a partial delithiation process is observed, without reaching the pristine composition (Fig. 10). This observation is in line with the electrochemical study, showing that the amount of deinserted lithium is significantly smaller than the inserted one. Fig. 13 shows the *in situ* evolution of the XRD patterns collected in the potential window [3-0.02 V]. For more clarity, only an expanded view of the region corresponding to (200) and (12-1) intense peaks is represented. If the first process (Process I) up to 1 inserted Li^+ could be attributed to a biphasic transition, two more processes can be identified after inserting more than 1 Li^+ . Within the composition range $1.0 \leq x \leq 2.0$, almost no change is observed in the diffraction pattern. This result suggests that the $\text{LiFe}_{0.5}\text{TiOPO}_4$ structure is stable in this range (process II). The growth of the SEI layer on the surface of the particles, on discharging to low voltage, is proposed to be a possible source of lithium consumption at this voltage range. Between $x = 2$ and $x \sim 3$, a progressive broadening of all diffraction profiles is observed, leading to extremely broad peaks after the insertion of more than 3 Li^+ , revealing the material structure degradation. This character is maintained also during the delithiation (charge) as shown by the XRD patterns (Fig. 13, bottom).

Ti K-edge XANES spectra collected in the voltage range [3-1.3 V] are shown in Fig. 14. During this process, a strong shift of the absorption edge towards lower energies is accompanied to the strong decrease in intensity of the pre-edge peak. The first observation is in line with the reduction of the titanium atoms upon lithium insertion. The strong intensity of the initial pre-edge peak corresponds well to the very distorted octahedral environment of the TiO_6 octahedra. A decrease of its intensity most probably is caused by a change of the coordination of the titanium centers, with a probable decrease of their distortion.

3.3. Electrochemical performances

The electrochemical performances of the Li//Fe_{0.5}TiOPO₄/C cells have been studied in the potential ranges of [3.0-1.3 V] see Fig 15 (a) and (b), and [3.0-0.02 V] see Fig 15 (c) and (d). Fe_{0.5}TiOPO₄/C electrodes cycled in the voltage range [3.0-1.3 V], exhibit good capacity retention at different current rates. For instance, a reversible capacity of 103 mAh.g⁻¹ can be retained after 30 cycles at C/2 rate with approximately 99.7% coulombic efficiency (Fig. 15b). In addition, excellent electrochemical performances of Fe_{0.5}TiOPO₄/C are observed in a broader voltage range [3.0-0.02 V]. A high specific capacity of 420 mAh.g⁻¹ at C/2 rate was achieved for the 30th cycle. This good performance was maintained even for the faster rate of 5C by delivering a specific capacity of 255 mAh.g⁻¹ at the 30th cycle (see Fig. 15c). Furthermore, a high coulombic efficiency of around 99.5% can be reached at C/2 rate after 50 cycles (see Fig. 15d). As shown, owing to the synthesis method and high purity of the pristine material Fe_{0.5}TiOPO₄/C, the electrochemical performances are better when compared to reported studies on this material [18, 21, 22].

Conclusion

We present a novel study of 3-D transition metal titanium-oxyposphate Fe_{0.5}TiOPO₄ that has been prepared by a facile sol-gel method followed by the carbon-coating process. The Fe_{0.5}TiOPO₄/C composite displays excellent Li storage properties with considerable capacity of 250 mAh.g⁻¹ after 50 discharge/charge cycles at 5C rate. The Fe_{0.5}TiOPO₄/C composite reveals enhanced electrochemical performances and high cycling stability compared to those prepared using the solid-state method [18].

Structural changes upon lithium ion insertion/extraction in Fe_{0.5}TiOPO₄/C electrode material, cycled in the [3-1.3 V] voltage window, is investigated by an *in situ* XRD study, showing the formation of new phase LiFe_{0.5}TiOPO₄. The participation of the titanium ions to the redox activity in this potential range [3.0-1.3 V] was clarified by *in situ* XANES.

1 From the electrochemical-behavior point of view, when discharging to lower voltage cut-off,
2 the discharge profile shows a large pseudo-plateau below 0.8 V (process II), which
3 corresponds to the insertion of a large number of lithium ions. In addition, a polarization
4 between the discharge and charge is observed, which may reflect the existence of different
5 processes between the insertion and extraction of lithium ion. Further, the *in situ* XRD
6 analysis shows a strong structural degradation of the electrode material at low voltage
7 domain.
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9 According to these characteristics and to the previously published investigations [18, 23, 31,
10 38], we suggest that the reaction mechanism of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ as anode material for Li-ion
11 batteries occurs in two steps: i) the lithium intercalation in $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ during the first
12 pseudo-plateau (process I), ii) the electrode material undergoes a conversion reaction during
13 the insertion of lithium at lower voltage (process II), in which a strong morphological and
14 structural reorganization is marked.
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16 **Acknowledgements**

17 The authors would like to thanks IRESEN-Morocco and CNRST for the financial support. A.
18 Mahmoud acknowledges the Forschungszentrum Jülich for an international postdoctoral grant.
19 ELETTRA Trieste is acknowledged for providing beamtime at beamline XAFS.
20 Antonella Iadecola, Guiliana Aquilanti and Luca Olivi are gratefully acknowledged for
21 expert advice on beamline.
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Figure captions

Fig. 1 X-ray diffraction patterns of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ refined with the Rietveld method.

Fig. 2 (High) View along the c axis, (Down) $\text{Ti}-\text{O}_1-\text{Ti}-\text{O}_1-$ chain in $\text{Fe}_{0.5}\text{TiOPO}_4$ structure.

Fig. 3 TGA curves of coated and non-coated $\text{Fe}_{0.5}\text{TiOPO}_4$.

Fig. 4 Raman spectra of (a) non-coated and (b) coated $\text{Fe}_{0.5}\text{TiOPO}_4$.

Fig. 5 First discharge-charge curves of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ achieved at C/10 rate in voltage range [3.0-0.02V].

Fig. 6 The 1st, 2nd, 10th and 40th discharge-charge curves of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ recorded at C/10 rate, in voltage range [3.0-0.02V].

Fig. 7 First discharge-charge curves of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ achieved at C/10 rate in different voltage range [3.0-1.3V], [3.0-0.5V] and [3.0-0.02V].

Fig. 8 The 1st, 2nd and 10th discharge-charge curves of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ achieved at C/10 rate in voltage range [3.0-1.3V].

Fig. 9 The 1st, 2nd and 10th discharge-charge curves of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ achieved at C/10 rate in voltage range [3.0-0.5V].

Fig. 10 The first cycle voltage-composition profile of $\text{Fe}_{0.5}\text{TiOPO}_4\text{-C//Li}$ cell between 3.0 V and 1.3V at a C/10 rate with the *in situ* XRD patterns recorded every 0.1 Li^+ ion/f.u insertion/extraction.

Fig. 11 Experimental and calculated profiles for the Le Bail fit of $\text{LiFe}_{0.5}\text{TiOPO}_4/\text{C}$ (electrode discharged to 1.3 V). The Bragg-position of the pristine material $\text{Fe}_{0.5}\text{TiOPO}_4\text{-C}$ are also shown for comparison.

Fig. 12 Monoclinic unit cell parameters evolution as a function of lithium amount during the first discharge to 1.3 V.

Fig. 13 Expanded view (200 and 11-2 peaks) of the lithium composition-dependent X-ray powder diffraction patterns of $\text{Li}_x\text{Fe}_{0.5}\text{TiOPO}_4$, during the first cycle with the voltage window [3.0-0.02V].

Fig. 14 *In situ* Ti K-edge XANES spectra measured during lithiation of $\text{Fe}_{0.5}\text{TiOPO}_4$ in the potential range [3-1.3 V].

Fig. 15 Capacity retention behavior of $\text{Fe}_{0.5}\text{TiOPO}_4/\text{C}$ electrodes with cycle number, at different rates in voltage range (a) [3.0-1.3V] and (c) [3.0-0.02V]. Coulombic efficiency with cycle number at C/2 rate in the voltage range (b) [3.0-1.3V] and (d) [3.0-0.02V]

Table 1 Atomic coordinates in Fe_{0.5}TiOPO₄/C

Fe _{0.5} TiOPO ₄ (Z = 4) ; P2 ₁ /c					
a = 7.3889(8) Å b = 7.3874(8) Å c = 7.4128(8) Å β = 120.405(6)°					
Atome	Wyckoff	x(Å)	y(Å)	z(Å)	Occ.
Fe	2a	0.0000	0.0000	0.0000	0.5
Ti	4e	0.7349 (3)	0.2226 (3)	0.5278 (3)	1
P	4e	0.2518 (5)	0.1240 (4)	0.7473 (5)	1
O1	4e	0.7512 (7)	0.1434 (7)	0.7616 (8)	1
O2	4e	0.7738 (8)	0.0161 (8)	0.1077 (1)	1
O3	4e	0.4396 (7)	0.2379 (1)	0.8766 (7)	1
O4	4e	0.2633 (2)	0.0187 (8)	0.5848 (8)	1
O5	4e	0.0752 (3)	0.2433 (1)	0.1512 (7)	1

Table 2 Main structural parameters of Fe_{0.5}TiOPO₄/C, < cation-O > is the average of the distances between the cation (P, Ti, Fe) and the oxygen atoms.

Fe-O (Å)		Ti-O (Å)		P-O (Å)	
Fe-O5	2x 2.04(3)	Ti-O1	1.78(3)	P-O4	1.47(3)
Fe-O1	2x 2.08(2)	Ti-O3	1.90(2)	P-O3	1.49(3)
Fe-O2	2x 2.19(3)	Ti-O4	1.97(2)	P-O5	1.50(3)
		Ti-O2	2.00(2)	P-O2	1.57(3)
		Ti-O5	2.21(2)		
		Ti-O1	2.26(3)		
< Fe-O > = 2.103 Å		< Ti-O > = 2.02 Å		< P-O > = 1.508 Å

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