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Structural changes upon lithium insertion in $\text{Ni}_{0.5}\text{TiOPO}_4$

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Nickel titanium oxyphosphate $\text{Ni}_{0.5}\text{TiOPO}_4$ (NTP), was prepared by co-precipitation route. Its structure was determined by single crystal X-ray diffraction. The compound crystallizes in the monoclinic system, S.G: $P2_1/c$ [$a = 7.333(1) \text{ \AA}$, $b = 7.316(2) \text{ \AA}$, $c = 7.339(2) \text{ \AA}$, $\beta = 119.62(3)^\circ$, $Z = 4$, $R_1 = 0.0142$, $wR_2 = 0.0429$]. The structure might be described as a $\{\text{TiOPO}_4\}$ framework made of corner-sharing $[\text{TiO}_6]$ octahedra chains running parallel to $[001]$ and cross linked by phosphate $[\text{PO}_4]$ tetrahedral, where half of octahedral cavities created are occupied by Ni atoms, and the other half of octahedral sites are vacant. During the first discharge, the NTP electrode delivered a capacity of 530 mAh/g, upon cycling within 0.5–4 V. To understand the electrochemical reaction mechanism using different characterization techniques viz. in situ synchrotron diffraction. Reciprocal magnetic susceptibility (χ^{-1}) of NTP, between 4 and 300 K, shows an almost linear behavior and can be fitted by the simple Curie–Weiss law.

1. Introduction

Recently, the rapid advances of science and technology became the engine for great industrial and economic growth. Through this growth the people of developed countries came to enjoy comfortable and convenient way of life. Electric power is the key energy source in a current and future society, which supports the life of ease and the world's socioeconomic system. As symbolized by the recent rapid growth in the use of compact communications tools, computers and other electronic devices, it is also evident that batteries, particularly secondary batteries, have become an essential part of our electricity-dependent day and age. The common basic structural unit of phosphates materials is $[\text{PO}_4]$. A varying condensation of such groups results in several structural families. The chemical and thermal stabilities ensure their utility both in fundamental and industrial uses, if only to quote: nonlinear optical properties, ferroelectricity, magnetism, laser properties, materials

for heterogeneous catalysis activity, thermal expansion properties [1–5]. Moreover, introduction of titanium to metal phosphate compounds may result in a rich structural diversity. Generally, the obtained compounds exhibit three-dimensional structures with dense phases synthesized at high temperatures like the $\text{M}_x\text{TiO}(\text{PO}_4)$ ($x = 1$ alkali metal [6,7]; $x = 0.5$ transition metal [8–12]) and $\text{Sr}_2\text{TiO}(\text{PO}_4)_2$ [13]. In all the above mentioned structures, the Ti atom adopts an octahedral geometry $[\text{TiO}_6]$. Of particular applications, materials with $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox pair are continuously tested as cathode materials. In fact, research for materials that would provide lighter batteries with higher energy density is the consequence of increasing demands on numerous portable devices like cell phones, computers and all emerging green technologies such as wind and solar technologies or hybrid and plug-in electric vehicles. During the recent years, and subsequent to the pioneer work of Padhi et al. [14], the development of new generation of cathode materials for Li rechargeable batteries started on the choice of 3d metals with the structure essentially feature to intercalate/de-intercalate Li ions reversibly. The originality in such materials, compared to the corresponding oxides, is the relatively high Li ion conductivity and increased working voltage, which is caused by the inductive effect of phosphate groups. In fact, the later decrease the covalence character of the bond $\text{M}-\text{O}$, which results in a decreasing of the potential of $\text{M}^{n+}/\text{M}^{(n-1)+}$ pair with respect to Li^+/Li . Researchers focused mainly to cheap and non

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Fig. 1. X-ray powder diffraction profiles of $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$ experimental (· · ·) and calculated patterns (—).

toxic iron-phosphates with Olivine [LiFePO_4], commonly known as LFP [15] and Nasicon [$\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$] [16]. LFP is one of the most promising cathode materials for lithium ion rechargeable batteries. It has a high theoretical specific capacity (170 mAh/g) and operating potential (3.45 V vs. Li^+/Li), greater as that from $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ (2.8 V). Early in 1970, TiS_2 has been used as a cathode material in commercial rechargeable lithium batteries, which operate at 2.1 V. Then after, good reversibility of $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple was found in Nasicon-like phosphates, such as $\text{LiTi}_2(\text{PO}_4)_3$ [17]. Later, several other lithium phosphates, silicates and sulfates have been also studied as insertion materials for lithium-ion batteries [18–21]. Recently, a new class of lithium insertion compounds, by investigating the ternary diagram of $\text{MO}-\text{TiO}_2-\text{P}_2\text{O}_5$ ($\text{M}=\text{Cr}^{2+}$, Co^{2+} , Ni^{2+} , etc.) have been reported [22–25]. Particularly Belharouak and Amine [22] early proposed $\text{Ni}_{0.5}\text{TiOPO}_4$ as a new lithium insertion material for Li-ion batteries with a significant capacity of 155 mAh/g. As to continue the investigations on such materials, we recently reported on $\text{Co}_{0.5}\text{TiOPO}_4$ [23] and on the core-shell $\text{Ni}_{0.5}\text{TiOPO}_4/\text{C}$ composites as anode materials in Li ion batteries [24], which was also published by Maher et al. [25], with a better capacity of 276 mAh/g [24]. According to these studies, oxyphosphates $\text{M}_{0.5}\text{TiOPO}_4$ ($\text{M} = 3d^{2+}$ ion) could act as electrodes for lithium batteries that provide high energy density. An analysis of their crystal structures shows that, hypothetically, up to three lithium atoms could be inserted per formula unit, generating thus an initial practical capacity of 434 mAh/g, which suggest that such phases could be used in low voltage, high energy density cells [22–25]. This high observed capacity and the fairly good cycling characteristics of the cell qualify this system to be a promising candidate for applications requiring high energy density at medium voltages. This finding has initiated a systematic study of mixed transition-metal phosphates and titanium [22–25]. During our structural investigations of the title compound, the crystal structure has been published [26]. We took on account our own data (see deposited crystal data deposited by ICSD [CCDC 417788]) in the calculations and correlations.

2. Experimental

2.1. Sample preparation

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ were selected as the starting materials in stoichiometric amount. Firstly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ were dissolved in diluted nitric acid solution, and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was dissolved in ethanol (1:4 vol.%). The mixture was stirred for hours and a green powder deposited which was dried at 60°C . The resulting powder was calcined progressively at 450°C for 12 h and 950°C for 24 h in air with intermittent grinding. The refined X-rays diffraction pattern of the end-product is depicted in Fig. 1. As matter of comparison, we report in Fig. 2 the XRPD of the series of oxyphosphates $\text{M}_{0.50}\text{TiO}(\text{PO}_4)$ ($\text{M}=\text{Cr}$, Mn , Fe , Co , Ni).

Fig. 2. The powder XRPD patterns of the $\text{M}_{0.50}\text{TiO}(\text{PO}_4)$ ($\text{M}(\text{II}) = \text{Mn}$, Fe , Ni , Co , Cr).

Table 1
Crystal data of $\text{M}_{0.50}\text{TiO}(\text{PO}_4)$ compounds at room temperature.

M^{II}	$r_{\text{M}^{2+}}(\text{\AA})$	S.G	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$	β°	Ref.
Mn- α	0.83	P2 ₁ /c	7.388(1)	7.367(1)	7.375(1)	120.34(2)	[38]
Mn- β	0.83	C2/c	8.84	6.53	7.17	113.06	[38]
Co- α	0.745	P2 ₁ /c	7.388(1)	7.367(1)	7.375(1)	120.34(2)	[23]
Co- β	0.745	P2 ₁ 2 ₁ 2 ₁	7.3520(1)	7.3520(1)	12.783(1)	90	[38]
Fe- α	0.780	P2 ₁ /c	7.4069(3)	7.3838(3)	7.4083(3)	120.36(1)	[27]
Fe- β	0.780	C2/c	13.337(3)	13.174(3)	8.6970(1)	100.10(3)	[38]
Ni	0.690	P2 ₁ /c	7.383(5)	7.323(5)	7.344(5)	120.23(6)	[38]
Cr	0.730	P2 ₁ /c	7.561(1)	7.092(1)	7.487(1)	122.25(1)	[38]

Table 2
Summary of crystal data and structure refinements for NTP.

Formula	$\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$
Formula weight	376.45 g/mol
Temperature	302(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2 ₁ /c
Unit cell dimensions	$a = 7.3330(10)$ Å $b = 7.316(2)$ Å $c = 7.339(2)$ Å $\beta = 119.62(3)^\circ$
Volume	$342.27(14)$ Å ³
Z, calculated density	2, 3.653 g/cm ³
Crystal size	0.28 mm × 0.14 mm × 0.06 mm
Scan method	ω -2 θ
Absorption coefficient	5.513 mm ⁻¹
$R(000)$	364
Theta range for data collection	3.20–26.37°
Index ranges	$-9 \leq h \leq 8, -9 \leq k \leq 8, -9 \leq l \leq 9$
Reflections collected [$I > 2\sigma(I)$]	2174
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	685/0/71
Goodness of fit on F^2	1.108
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0530, wR_2 = 0.0525$
R indices (all data)	$R_1 = 0.0202, wR_2 = 0.0190$
Extinction coefficient	0.173(6)

Moreover, we summarize in Table 1 cell parameters of the isoformular compounds in this series.

Single crystals were prepared by melting the resulting powder at $1250 \pm 20^\circ\text{C}$ and slow cooling in a platinum crucible. The melt was held at this temperature during 8 h, cooled to 500°C at rate of 3°C/h and finally to room temperature by just turning off the furnace power. A mixture of dark green and yellow-green crystals was obtained. According to their XRPD patterns, they correspond respectively to $\text{Ni}_{0.5}\text{Ti}_2(\text{PO}_4)_3$ and $\text{Ni}_{0.5}\text{TiOPO}_4$.

2.2. Material characterizations

Single crystal of NTP, with dimensions of $0.15 \text{ mm} \times 0.21 \text{ mm} \times 0.30 \text{ mm}$, was selected for single-crystal X-ray diffraction determination. Data collections were performed on a Gemini of Oxford Diffraction CCD diffractometer with graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å) radiation using the $\omega/2\theta$ scan mode at 302(2) K. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [27,28]. Crystallographic data and structural refinements for the compound are summarized in Table 2. The atomic coordinates and thermal parameters are listed in Table 3. Important bond distances are listed in Table 4.

Table 3
Atomic positions and equivalent isotropic displacement parameters ($\times 10^3 \text{ \AA}^2$) for NTP.

Atom	x	y	z	U (eq)
Ni1	0.5	0.0	0.0	4.6(2)
Ti1	0.23530(6)	-0.27845(6)	-0.29510(6)	3.4(2)
P1	0.25459(8)	-0.62393(8)	0.00500(9)	3.2(2)
O(1)	0.2409(3)	-0.5097(2)	-0.1755(3)	7.9(4)
O(2)	0.5551(3)	-0.2478(2)	-0.0907(3)	6.5(4)
O(3)	-0.0582(3)	-0.2389(2)	-0.4294(3)	8.5(4)
O(4)	0.7169(3)	0.0030(2)	0.3150(3)	6.4(4)
O(5)	0.7330(2)	0.1554(2)	0.0010(3)	6.9(4)

Supplementary data of crystal structures and refinements, especially full bond lengths, angles and anisotropic thermal parameters, have been deposited [CCDC 417788]. These data can be obtained from ICSD (details of the procedure, see: www.ccdc.cam.ac.uk).

2.3. Electrochemical measurements

Electrochemical measurements were performed in Li test cells assembled in an argon-filled glove box. Test electrodes were prepared by mixing active material, acetylene black, and polytetrafluoroethylene (PTFE) binder with a weight ratio of 75:20:5. The mixture was compressed into sheets and cut into circular strips of 8 mm in diameter, and then loaded on Cu foil. The cells were assembled after the strips were dried at 100°C overnight. Lithium foil was used as counter and reference electrodes. A solution of 1 mol/L LiPF₆ dissolved in ethylene carbonate (EC)–ethyl methyl carbonate (EMC)–dimethyl carbonate (DMC) (1:1:1 vol.%) was used as the electrolyte. The discharge/charge cycling tests were performed on Land CT2001 battery testers with a voltage range of 0.5–3.0 V. Cyclic voltammetry (CV) was conducted on a CHI 600A electrochemical analyzer with a scan rate of 0.1 mV/s in the potential range of 0.5–3 V (vs. Li/Li⁺).

In situ synchrotron diffraction was performed at the powder diffractometer B2 HASYLAB/DESY (Hamburg, Germany). The diffraction patterns were collected with an on-site readable image plate detector. The wavelength $\lambda = 0.49324$ Å was selected with a Si(111) double-crystal monochromator. Rietveld analyses, based on the synchrotron data, were performed with the software package Fullprof.

The synthesis of $\text{Li}_x\text{Ni}_{0.5}\text{TiOPO}_4$ with $x = 0.5$ and 1 was performed by ion exchange method starting from NTP. Lithium intercalation into this phase has been carried out electrochemically using Swagelok type cells.

Table 4
Selected bond lengths (Å) and bond angles ($^\circ$) for NTP.

Ni—O(2)	2.039(2)	Ni—O(2) ⁱ	2.039(2)
Ni—O(5)	2.049(2)	Ni—O(5) ^j	2.049(2)
Ni—O(4)	2.059(2)	Ni—O(4) ^j	2.059(2)
Ti—O(5) ⁱⁱⁱ	1.7087(17)	P—O(3) ⁱⁱⁱ	1.5163(18)
Ti—O(3)	1.8950(18)	P—O(1)	1.5269(18)
Ti—O(1)	1.8971(17)	P—O(2) ^v	1.5350(17)
Ti—O(4) ^j	2.0629(17)	P—O(4) ^{iv}	1.5419(18)
Ti—O(2)	2.0790(19)		
Ti—O(5) ^j	2.2421(18)		
O2 Ni1 O2	180.0	O(3)—Ti—O(2)	160.98(14)
O2 ⁱ Ni1 O5 ⁱ	101.24(7)	O(1)—Ti—O(2)	89.22(14)
O2 Ni1 O5 ⁱ	78.76(7)	O5 Ti1 O2 ⁱⁱ	94.05(8)
O2 ⁱ Ni1 O5	78.76(7)	O3 Ti1 O2	160.91(7)
O2 Ni1 O5	101.24(7)	O1 Ti1 O2	90.20(8)
O5 Ni1 O5 ⁱ	180.00(11)	O4 Ti1 O2 ⁱ	77.00(7)
O2 ⁱ Ni1 O4 ⁱ	102.04(6)	O5 ⁱⁱ Ti1 O5 ⁱ	166.05(8)
O2 Ni1 O4 ⁱ	77.96(6)	O3 Ti1 O5 ⁱ	89.43(8)
O5 ⁱ Ni1 O4 ⁱ	79.05(7)	O1 Ti1 O5 ⁱ	86.82(7)
O5 Ni1 O4 ⁱ	100.95(7)	O4 ⁱ Ti1 O5 ⁱ	74.67(7)
O2 Ni1 O4 ⁱ	77.96(6)	O2 Ti1 O5 ⁱ	73.68(7)
O2 Ni1 O4	102.04(6)		
O5 Ni1 O4 ⁱ	100.95(7)		
O5 Ni1 O4	79.05(7)		
O4 Ni1 O4 ⁱ	180.00(12)	O3 P1 O1 ⁱⁱⁱ	110.06(10)
O5 Ti1 O3 ⁱⁱⁱ	101.49(8)	O3 ⁱⁱⁱ P1 O2 ^v	108.51(10)
O5 Ti1 O1 ⁱⁱ	100.09(8)	O1 P1 O2 ^v	110.29(10)
O3 Ti1 O1	97.83(8)	O3 ⁱⁱⁱ P1 O4 ^{iv}	110.47(10)
O5 ⁱⁱ Ti1 O4 ⁱ	96.42(8)	O1 P1 O4 ^{iv}	109.64(10)
O3 Ti1 O4 ⁱⁱ	90.18(7)	O2 ^v P1 O4 ^{iv}	107.82(10)
O1 Ti1 O4 ⁱ	159.78(8)	O(2)—P—O(4)	107.97(18)

Symmetries code: (i) $1 - x, y, -z$; (ii) $1 - x, y + 1/2, -z + 1/2$; (iii) $-x, y - 1/2, -z - 1/2$; (iv) $1 - x, y - 1/2, -z + 1/2$; and (v) $1 - x, -1 - y, -z$.

Fig. 3. $[\text{TiO}_6]$ octahedra running parallel to the c axis in the structure of NTP, face sharing from $[\text{NiO}_6]$ and $[\text{TiO}_6]$ leads to trimmers $[\text{Ti}_2\text{NiO}_{12}]$.

3. Results and discussion

3.1. Structure description

The dominant structural units in the oxyphosphate NTP are chains made from corner sharing $[\text{TiO}_6]$ octahedra running parallel to the c axis (Fig. 3). The O(1) oxygen atoms of the shared corners, not implied in $[\text{PO}_4]$ tetrahedra, justify the oxyphosphate designation. The $[\text{TiO}_6]$ groups in NTP show their typical KTP-type distortion mode, in which the titanium atom makes a nominal displacement from the center of its octahedron along a Ti–O bond axis, which results in short (1.713 Å) bond formed between Ti and O(1). Each Ti center makes two Ti–O–Ti bonds (via O(1)) and four Ti–O–P ones. Titanium octahedra chains are linked by phosphate tetrahedra $[\text{PO}_4]$ to constitute sheets parallel to ab -plane. Inside this framework, Ni atoms occupy the cavities and this association results in trimmers $[\text{Ti}_2\text{NiO}_{12}]$ made from face sharing $[\text{NiO}_6]$ and $[\text{TiO}_6]$ (Fig. 3). Ni atoms occupy one position in $\text{Ni}_{0.50}\text{TiO}(\text{PO}_4)$, mean (Ni–O) distances in the corresponding $[\text{NiO}_6]$ octahedral are respectively 2.051, 2.062 and 2.042 Å. In each case, it is less than the ionic radii sum of O^{2-} and Ni^{2+} (2.10 Å), indicating a slight covalent character of the Ni–O bond. There is no way to envisage magnetic exchanges between Ni octahedra since they are isolated in the structure, with short $d(\text{Ni–Ni})$ distance of 5.181 Å, which is of the same magnitude as the values recently published [26], or even in the powder study [8]. Phosphate groups in NTP are typically regular ($\text{BVS}(\text{P}^{5+}) = 5.022$).

3.2. Electrochemical properties of NTP

Fig. 4 shows the first charge/discharge (D1, C1) curves of NTP between 0.5 and 4.0 V at the rate of 42.7 mA/g. During the first discharge, the NTP electrode delivered a capacity of 530 mAh/g. This high capacity is equivalent to the intercalation of more than 3.5 lithium ions per $\text{Ni}_{0.5}\text{TiOPO}_4$; however, not all the lithium atoms could be extracted during the subsequent charge [18,20,31]. Fig. 5 shows the initial CV curves of NTP with a potential range 0.5–4 V and a scan rate of 0.1 mV/s at 25 °C. The interesting feature is the difference between the first and second cycle. The first cathodic scan shows three reduction peaks. A major peak

centered at 1.43 V corresponding to titanium reduction (from Ti^{4+} to Ti^{3+}), a medium at 1.24 V may be attributed to nickel reduction and a minor one, located at 0.80 V, corresponds to the reduction of the electrolyte components at the electrode surface leading to the well known solid electrolyte interfacial (SEI) film formation. In the 2nd and 3rd cycles, the reduction and oxidation processes show only one cathodic and one anodic peaks appearing at 1.06 V and 2.24 V and at 1.006 V and 2.26 V, respectively, which are attributed to the $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple. In order to examine the preliminary life performance of NTP composite, 10 cycles charge/discharge were carried out at low-rate. For NTP, in a first approach, the plateau at 1.45–1.25 V, $x=0$ –1 (Fig. 4), would correspond to a monophasic domain surrounded by solid-solution regions of both extremes between $\text{Ni}_{0.5}\text{TiOPO}_4$ and $\text{LiNi}_{0.5}\text{TiOPO}_4$ (labeled I) (Figs. 6 and 7), this probably means that only one

Fig. 4. The first charge/discharge curves of $\text{Ni}_{0.5}\text{TiOPO}_4$ measured at 42.7 mA/g in the potential range of 0.5–4.0 V.

Fig. 5. The initial three-cycle CV curves of NTP.

Fig. 8. RPE of $\text{Li}_x\text{Ni}_{0.5}\text{TiOPO}_4$, $x = 0.25, 0.5, 0.75$ and 1 .

Fig. 6. Diffraction pattern collected at different amount of lithium during the first in situ discharge cycle C/5 of $\text{Ni}_{0.5}\text{TiOPO}_4$ vs Li/Li^+ .

structural/electronic phenomenon is involved during the first irreversible lithium insertion. Furthermore, it is well known that $\text{Ti}^{4+}/\text{Ti}^{3+}$ couple is active around 1.5 V as observed in same electrode materials such as $\text{Co}_{0.5}\text{TiOPO}_4$ [23a,b]. The concentration of Ti^{3+} , due to titanium reduction from Ti^{4+} to Ti^{3+} , is increased by

Lithium insertion as could be confirmed by the RPE spectrum shown in Fig. 8. The second process at 1.25–1.08 V (Fig. 4) is more complex, which probably includes a second biphasic domain (I + II). The third process at 1.08–0.7 V (Fig. 4) would correspond to a monophasic domain (labeled II). In order to understand the structural changes upon the 1st electrochemical lithium intercalation causing the high irreversible discharge capacity, synchrotron based in situ XRD experiments were performed to confirm the presence of two-phase domains (Figs. 6 and 7). These changes suggest the formation of new lithiated phases through a topotactic mechanism. The intensity of

the newly evolved peaks increases with increasing Li content, while few peaks almost vanish. These changes suggest the formation of new lithium insertion phases through a topotactic mechanism. Both phases crystallize in the monoclinic symmetry ($\text{P2}_1/\text{c}$), with the following parameters: $a = 7.135 \text{ \AA}$, $b = 7.723 \text{ \AA}$, $c = 7.321 \text{ \AA}$, $\beta = 119.37^\circ$ (I) and $a = 6.5612(4) \text{ \AA}$, $b = 8.0919(4) \text{ \AA}$, $c = 8.4874(4) \text{ \AA}$, $\beta = 122.25(1)^\circ$ (II). The results of refinement are illustrated in Fig. 9a and b. In fact, if the space group remains unchanged, the cell parameters vary anisotropically: a smooth contraction of the parameters a ($\sim 0.6 \text{ \AA}$) and c ($\sim 0.4 \text{ \AA}$), while b is more expanded ($\sim 1.17 \text{ \AA}$) passing from (I) to (II). Accordingly, the excess capacity of NPT in the subsequent cycles might be ascribed to $\text{Ni}^{2+}/\text{Ni}^0$ redox pairs according to a conversion or displacement mechanism [23]. However, from the synchrotron diffraction patterns of the electrode after the first discharge, the Ni^0 metallic

Fig. 7. 3D in situ X-ray diffraction patterns of a $\text{Li}/\text{Li}_x\text{Ni}_{0.5}\text{TiOPO}_4$ cell discharged at C/5 rate.

Fig. 9. (a and b) Synchrotron diffraction of the fresh battery cell.

Fig. 10. (a and b) Ex situ XRD patterns X-ray diffraction patterns of a $\text{Li}/\text{Li}_x\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$ cell discharged from 0.5 to 4 V at C/5 rate.

Fig. 11. (a and b) X-ray diffraction profiles of $\text{Li}_x\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$ with x = 0.5 (a) and 1 (b) experimental (dotted line) and calculated patterns (solid line).

Fig. 12. Hypothetical structure from $\text{Li}_{0.5}\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$, a projection onto (001) and (100).

phases could not be detected directly in the experiments, probably because of a too small size of the crystalline precipitations. Also, Belharouak et al. [22] failed to find any evidence of Ni^0 through the X-ray absorption near edge structure (XANES) due to the experimental complexity. In Fig. 10 a and b we report the ex situ DRX diagram of NPT. The peaks vanish progressively to the benefit of those of $\text{Li}_x\text{Ni}_{0.5}\text{TiOPO}_4$ with $x=0.5$ and 1 at smaller 2θ angles. Both phases are compatible with the proposed structure model obtained from that of NPT by an additional occupation of the (2a)-site at (0, 0, 0) with Li. The lattice parameters have been refined by the Rietveld method: $a=7.3219(6)\text{ \AA}$, $b=7.3322(5)\text{ \AA}$, $c=7.3432(6)\text{ \AA}$, $\beta=119.513(4)^\circ$ for $x=0.5$ (Fig. 11a) and $a=7.392(3)\text{ \AA}$, $b=7.391(3)\text{ \AA}$, $c=7.292(3)\text{ \AA}$, $\beta=117.699(17)^\circ$ for $x=1$ (Fig. 11b). The structure of $\text{Li}_{0.5}\text{Ni}_{0.5}\text{TiOPO}_4$ consists of a 3D anionic framework formed by chains of alternating TiO_6 octahedra and PO_4 tetrahedra sharing corners (Fig. 12). TiO_6 chains are linked together by phosphate tetrahedral. The lithium and nickel atoms occupy simultaneously 2a and 2b cavities. Titanium atom is displaced from the geometrical center of the octahedron resulting in alternating of short (1.711 Å) and long (2.271 Å) Ti–O bonds. The four remaining Ti–O bond distances have intermediate values ranging between 1.908 and 2.056 Å. Average The $d_{\text{av}}(\text{Ti}-\text{O})$ in the $[\text{TiO}_6]$ octahedron is 1.983 Å, which is in good agreement with the ionic radius sum [36]. These distances are comparable to those found in $\text{M}_{0.5}\text{TiOPO}_4$, $\text{M}=\text{Mn}, \text{Co}$ and Ni , oxyphosphates series and $\text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4$. The Li/Ni atoms are coordinated to six oxygen. Li/Ni–O bond distances vary between 2.038 and 2.215 Å in $[(\text{Li}/\text{Ni})\text{O}_6]$ octahedral. Average Li/Ni–O distances [$d_{\text{av}}(\text{Li})-\text{O}$: 2.169 Å, $d_{\text{av}}(\text{Ni})-\text{O}$: 2.132 Å for $x=0.5$ and $d_{\text{av}}(\text{Li})-\text{O}$: 2.169 Å, $d_{\text{av}}(\text{Ni})-\text{O}$: 2.132 Å for $x=1$ respectively]. The Lithium and Nickel octahedra are located between $[-\text{Ti}-\text{O}-\text{Ti}-]$ chains; share all faces with TiO_6 octahedra. They are linked together by common edges (O_1-O_2) and form infinite chains along a -axis. The $[\text{PO}_4]$ tetrahedra strengthen the framework $[\text{TiOPO}_4]^-$ by sharing all corners with Ti polyhedra (Fig. 12). The average $\langle \text{P}-\text{O} \rangle$ is of the same range as in the $\text{Li}_x\text{Ni}_{0.5}\text{TiOPO}_4$ 1.52 for $x=0.5$ and 1.52 for $x=1$, respectively and also to compare with what is reported by Corbridge for orthophosphates, 1.53 Å [37].

3.3. Magnetic characterization

The magnetic susceptibility (χ) of $\text{Li}_x\text{Ni}_{0.5}\text{TiOPO}_4$ with $x=0, 0.5$ and 1 as a function of temperature is shown in Fig. 13. The $\chi(T)$ data

Fig. 13. Thermal evolution of the magnetic susceptibility (χ) of $\text{Li}_x\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$ with $x=0, 0.5$ and 1.

could be fitted to Curie–Weiss law in the range 4–300 K. It shows an almost linear behavior and can be fitted by the simple Curie–Weiss equation $\chi = C/(T - \theta_c)$. The Curie constant $C = 2.83 \text{ emu mol}^{-1} \text{ K}^{-1}$ corresponding to an effective magnetic moment $\mu_{\text{eff}} = 3.32 \mu_B/\text{f.u.}$, which is in agreement with the expected theoretical value (generally from $\mu_{\text{eff}} = 2.9\text{--}3.4 \mu_B/\text{f.u.}$) originating from spin contribution only considering ions Ni^{2+} (d^8 , HS). For $\text{Li}_{0.5}\text{Ni}_{0.5}\text{TiOPO}_4$ the corresponding effective moment is found to be $\mu_{\text{eff}} = 3.84 \mu_B/\text{f.u.}$ This value is corresponding to half Ni^{2+} and half Ti^{3+} in the formula unit. For the $\text{LiNi}_{0.5}\text{TiOPO}_4$ the experimental effective moment may correspond to half Ni^{2+} and one Ti^{3+} in the formula unit ($\mu_{\text{eff}} = 4.25 \mu_B/\text{f.u.}$). The data here published in the present work will be included in the thesis from Essehli [38].

4. Conclusions

In this work we have investigated $\text{Ni}_{0.5}\text{TiO}(\text{PO}_4)$ (NTP) as possible negative electrodes in Li-ion battery. The structure of NTP is isostructural to that of the $\text{M}_{0.5}\text{TiO}(\text{PO}_4)$ series with $\text{M}=\text{Cr}, \text{Mn}, \text{Fe}$ and Co . A reinvestigation of its crystal structure was performed

to correlate the physicochemical investigations. For NTP, we found that, rather than reacting with 1 Li⁺ by reduction of Ti⁴⁺ to Ti³⁺ as one would expect from the structure, this compound reacts with 3.5 Li⁺ during the first lithiation. During the following cycles, 2 Li⁺ are reversibly intercalated/deintercalated in the structure. The lithium intercalation properties of NTP and Li_xNi_{0.5}TiO(PO₄) were studied. For the later system, structural changes in dependence on the quantity of inserted Li in the framework of Ni_{0.50}TiO(PO₄) were reported. Magnetic properties have been correlated with the structural ones.

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