Synthesis and characterization of carbon-coated Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ anode material

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1. Introduction

At the present time, considerable effort is applied for the development of new electric energy sources and improvement of the already known systems. In particular, great attention is focused on rechargeable Li-ion batteries. Many materials have been extensively studied as positive electrodes for lithium batteries, such as LiCoO$_2$ [1–3], LiNiO$_2$ [4,5] and LiFePO$_4$ [6–10]. LiCoO$_2$ shows a stable electrochemical performance over hundreds of cycles, but it delivers only half of the theoretically possible capacity. In addition, this material is expensive and not environmentally friendly. LiNiO$_2$ is an attractive cathode material because of its comparatively low cost, high theoretical capacity and environmental advantages compared to LiCoO$_2$ [11,12]. But it is extremely difficult to synthesize in reproducible conditions and the cycling behaviour is poor at high voltages.

Extensive research was also devoted to understanding and improving existing anode materials in today’s lithium ion batteries. The most commonly used material is graphite [13]. Parallel to this, there is a great incentive to find new negative electrode materials that can store more lithium or function more safely than graphite. Among the developing material, the spinel Li$_4$Ti$_5$O$_12$ became an attractive alternative because it operates above the potential of lithiated graphite, thereby improving safety [14,15].

The experimental discharge capacity of this material is greater than 160 mAh/g.

Lithium transition metal phosphates are mainly used as positive electrode materials for Li-ion batteries. The existence of M$_n$(PO$_4$)$_y$ framework provides an excellent stability and long term cycling to this type of cathode in comparison to lithium transition metal oxides. Indeed, the oxygen–phosphorous bond is more covalent in nature than polar oxygen–metal bonds. Thus, no loss of oxygen occurs from the framework and the reactivity with the electrolyte is low [16]. Only one member of this class of materials, LiFePO$_4$, has become the answer to these requirements so far, also owing to other characteristics such as low cost, being environmentally benign and showing high safety. The main problem of LiFePO$_4$ lies in its poor rate capability, which is attributed to its low electronic conductivity and slow kinetics of lithium-ion diffusion through the LiFePO$_4$–FePO$_4$ interfaces [17,18].

Several other lithium transition metal phosphates, including LiTi$_2$(PO$_4$)$_3$ [19], Li$_3$Fe$_2$(PO$_4$)$_3$ [20], Li$_2$VOP$_2$O$_7$ [21], Ni$_{0.5}$TiOPO$_4$ [22] and Co$_{0.5}$TiOPO$_4$ [23], have been intensively studied over the world. Concerning the two later oxyphosphates, their electrochemical features (especially the working potential) qualify these systems either as anodes for 5 V lithium ion batteries or as cathodes for applications requiring high energy density for medium voltages.

In the quest for other new framework materials based on the phosphate polyanion building block, we have investigated the electrochemical properties of Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ oxyphosphate. Single crystals of this material were firstly prepared by Manoun et al. [24]. The main disadvantage of this family of materials is their poor intrinsic electronic conductivity, which restricts their potential use
as active material in Li-ion batteries. Fortunately, this problem could be solved by coating particles of the desired phosphate with carbon. Many different carbon sources are possible. Here, we use polyethylene glycol (PG) for the carbon-coating process.

In this paper, the carbon coated Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ has been synthesized by the co-precipitation method followed by the thermal treatment of the Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$–PG mixture at 500 °C under a reducing atmosphere. In this way, PG is completely converted into electronically conductive carbon. The obtained composite was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. The electrochemical behaviour of the material was also studied. Note that in order to evidence the effect of additional carbon, we have prepared and studied the pure Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ within the same conditions.

2. Experimental

Microcrystalline Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ was prepared from a stoichiometric mixture between an aqueous solution of LiNO$_3$ (99%, Aldrich), Ni(NO$_3$)$_2$·6H$_2$O (99%, Aldrich), and (NH$_4$)$_2$HPO$_4$ (98%, Merck) with a solution of TiCl$_4$ (99% Aldrich) diluted in ethanol. A slow addition of titanium solution in the aqueous mixture with constant stirring, at room temperature, induces the formation of precipitates. After evaporation at 45 °C under vacuum, the resulting powder was progressively heated in air at 400 °C for 12 h to allow for the decomposition of the phosphate precursor and at 900 °C for 12 h to complete the synthesis of the desired oxyphosphate. A fine green powder was then obtained. One part of this obtained powder was dispersed with 10% in mass of polyethylene glycol (PG) powder in acetone. After evaporating the acetone, the mixture was heated to 500 °C for 12 h in a flow of CO$_2$ gas (50:50).

The morphology of the samples was studied by scanning electron microscopy (SEM) using high resolution scanning electron microscopy (HRSEM LEO 1550).

The Raman spectra were collected at room temperature using a Renishaw 2000 spectrometer equipped with a 785 nm diode laser. Spectra were recorded in the 1900–100 cm$^{-1}$ range.

The positive electrodes were prepared by mixing 75% active material, 10% super-P carbon powder and 15% PVDF (polyvinylidene fluoride) binder in NMP (1-methyl-2-pyrrolidinone) solvent onto an aluminium foil. The coated aluminium was transferred onto an aluminium foil. The coated aluminium was transferred onto an aluminium foil and dried overnight in a vacuum oven at 120 °C. The cathode was assembled in a “coffee-bag” [25] (polymer laminated aluminium foil) type cell using a lithium foil as anode, an electrolyte of 1 M LiClO$_4$ in EC/DEC (Merck, battery grade and used as received) 2:1 by volume mixture and glass–wool separator. Charge–discharge tests were performed using a Digatron BTS 600 battery testing system with different rates and voltage cut-off positions at room temperature.

The cyclic voltammetry (CV) was carried out at 0.01 mV/s scanning rate in 0.5–4 V vs. Li/Li$^+$ potential range using VMP cycling system.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the XRD patterns of the Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ sample (referred to as LNTP) and the Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$–C composite (referred to as LNTPC). The diffraction lines were indexed in the monoclinic system (P2$_1$/c space group). However, two weak TiO$_2$ peaks were observed in the diffractograms. The Rietveld refinement of the XRD data in the hypothesis of the existence of two phases shows that the amount of the TiO$_2$ impurity was 4.7%.

The XRD pattern of the LNTP powder shows narrower diffraction lines comparing to LNTPC composite indicating better crystallinity with little difference between the observed and calculated patterns. Nevertheless, no significant difference in the unit cell parameters of the two studied materials has been evidenced. Note that no traces of carbon have been detected in the XRD pattern of the LNTPC composite. This implies that the residual carbon is in an amorphous state. The structural data and details of the refinement, performed by using the Rietveld method, are summarized in Table 1. While the refined atomic parameters for Li$_{0.5}$Ni$_{0.25}$TiOPO$_4$ are given in Table 2. Note that the obtained atomic positions agree well with those obtained by Manoun et al. [24].

Fig. 2 shows the structure of LNTP. It can be described as three-dimensional networks of TiO$_6$ and NiO$_6$ octahedra and PO$_4$ tetrahedra within which Li$^+$ ions are located. Each TiO$_6$ octahedron shares one face with one NiO$_6$ octahedron, while NiO$_6$ octahedron shares corners with four PO$_4$ and two other corners with two TiO$_6$ octahedra. Lithium atoms fully occupy the site 2a, whereas nickel atoms occupy statistically half of the site 2b. As can be seen, the Ti$^{4+}$ ions are isolated in the structure. This explains why the electronic conductivity (hopping mechanism) is very low in this phosphate.

3.2. Textural and morphology studies

Fig. 3a–d shows the SEM micrographs of the LNTP oxyphosphate and LNTPC composite at different magnification. The SEM micrographs clearly show the difference in the microstructures.
Table 1
Structural data and X-ray Rietveld refinement parameters of \( \text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4 \) and \( \text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4/C \).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( B (\text{Å}^2) )</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2a</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.38(3)</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni</td>
<td>2b</td>
<td>0.5000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.49(2)</td>
<td>0.50</td>
</tr>
<tr>
<td>Ti</td>
<td>4e</td>
<td>0.7563(6)</td>
<td>0.2196(4)</td>
<td>0.3337(5)</td>
<td>0.40(3)</td>
<td>1.00</td>
</tr>
<tr>
<td>P</td>
<td>4e</td>
<td>0.2608(1)</td>
<td>0.1299(1)</td>
<td>0.3738(2)</td>
<td>0.40(3)</td>
<td>1.00</td>
</tr>
<tr>
<td>O(1)</td>
<td>4e</td>
<td>0.7501(6)</td>
<td>0.1499(4)</td>
<td>0.1132(1)</td>
<td>0.29(2)</td>
<td>1.00</td>
</tr>
<tr>
<td>O(2)</td>
<td>4e</td>
<td>0.7414(3)</td>
<td>0.0028(1)</td>
<td>0.7941(4)</td>
<td>0.29(2)</td>
<td>1.00</td>
</tr>
<tr>
<td>O(3)</td>
<td>4e</td>
<td>0.2345(2)</td>
<td>0.4848(4)</td>
<td>0.0492(1)</td>
<td>0.29(2)</td>
<td>1.00</td>
</tr>
<tr>
<td>O(4)</td>
<td>4e</td>
<td>0.4522(2)</td>
<td>0.2594(2)</td>
<td>0.8639(2)</td>
<td>0.29(2)</td>
<td>1.00</td>
</tr>
<tr>
<td>O(5)</td>
<td>4e</td>
<td>0.9444(1)</td>
<td>0.7466(2)</td>
<td>0.1311(2)</td>
<td>0.29(2)</td>
<td>1.00</td>
</tr>
</tbody>
</table>

The particles of the LNTP/C composite have a granular shape with an average particles size of 0.7 μm. Some of these particles seem to be interconnected. For the pure LNTP, the morphology is different. Some aggregates larger than 4 μm are present in this powder. This difference in morphology will play an important role for the electrochemical performances. Indeed, the small particle size and the interconnection between particles induced by the presence of carbon will enhance the electronic conductivity of the LNTP/C composite. Thus, an improvement of the electrochemical performance compared to that of LNTP is expected.

### 3.3. Raman spectroscopy

Raman analysis was used essentially to confirm the presence of the carbon coating layer in the LNTP/C composite.

Vibrational analysis for an isolated PO43− anion with group Td leads to four modes: \( A_1 (\nu_1: \nu_3(\text{PO}_4)) \), \( E (\nu_2: \delta(\text{PO}_4)) \) and 2\( T_2 (\nu_3: \nu_{as}(\text{PO}_4) \) and \( \nu_4: \delta_{as}(\text{PO}_4) \). All of them are Raman active: \( \Gamma = A_1 + E + 2T_2 \).

Fig. 4 gives a comparison of the Raman spectra of LNTP and LNTP/C. The high frequency part (900–1100 cm\(^{-1}\)) those situated below 300 cm\(^{-1}\) corresponds to the stretching vibrations of the PO4 tetrahedra (\( \nu_1 \) and \( \nu_2 \)). The intense band observed at approximately 760 cm\(^{-1}\) is 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 subsequent cycles, the reduction and oxidation processes show only one cathodic and one anodic peaks centred at 1.4 V and 1.73 V, respectively which are attributed to the Ti4+/Ti3+ redox couple. This irreversibility during the first discharge (Li insertion) is consistent with the results evidenced in the galvanostatic cycling experiment shown in Fig. 6. Indeed, three voltage plateaus are detected during the first discharge at approximately the same voltages mentioned above. Whereas during the subsequent charge (Li extraction), only one voltage plateau at ~1.72 V remains.

It should be noticed that the theoretical capacity of \( \text{Li}_{0.5}\text{Ni}_{0.25}\text{TiOPO}_4 \) electrode material is given by \( Q_{\text{calc}} = 150 \Delta x \text{mAh}/g \) where \( \Delta x \) corresponds to the amount of the intercalated lithium-ions. Reduction of all active ions (Ni\(^{2+}\) and Ti\(^{4+}\)) involves the insertion of 1.5 lithium-ions corresponding

The cyclic voltametry (CV) curve of the LNTP/C composite for two cycles is shown in Fig. 5. The interesting feature is the difference between the first and second cycle. The first cathodic scan shows three reduction peaks. A major peak centred 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 subsequent cycles, the reduction and oxidation processes show only one cathodic and one anodic peaks centred at 1.4 V and 1.73 V, respectively which are attributed to the Ti4+/Ti3+ redox couple. This irreversibility during the first discharge (Li insertion) is consistent with the results evidenced in the galvanostatic cycling experiment shown in Fig. 6. Indeed, three voltage plateaus are detected during the first discharge at approximately the same voltages mentioned above. Whereas during the subsequent charge (Li extraction), only one voltage plateau at ~1.72 V remains.
Fig. 3. SEM micrographs of LNTP oxyphosphate (a and b) and LNTP/C composite (c and d).

Fig. 4. Comparison between the Raman spectroscopy curves of LNTP oxyphosphate and LNTP/C composite.

Fig. 5. The first two cyclic voltammograms of LNTP/C composite recorded in the 0.5–4 V voltage range. Scan rate: 0.01 mV/s.
to the Ti^{4+}/Ti^{3+} and Ni^{2+}/Ni redox couples. This implies that the theoretical capacity is equal to 225 mAh/g. This is an indication that the obtained experimental capacity during the first discharge (about 300 mAh/g) corresponds not only to the insertion of lithium-ions but also to the formation of the SEI interface. As shown in Fig. 6a, the plateau at ca 1.43 V corresponds to 147 mAh/g which corresponds to the reduction of one mole of Ti^{4+} ions ($\Delta x = 0.98$).

During the subsequent cycles, the capacity remains constant and approximately equal to 200 mAh/g. This implies that the main active redox couple during Li/Li$_0.5$Ni$_{0.25}$TiOPO$_4$ electrochemical cell cycling is Ti$^{4+}$/Ti$^{3+}$. The excess experimental capacity during cycling could be associated to the Ni$^{2+}$/Ni redox couple.

In order to examine the preliminary life performance of LNTP/C composite, 50 charge/discharge cycles were carried out at low-rate. Fig. 7 shows the charge/discharge curves of the Li/LNTP/C electrochemical cell cycled between 0.5 V and 3 V at a C/20 rate. The first discharge capacity was 307 mAh/g. On charge, the capacity decreased to 200 mAh/g losing about one third of its discharge capacity. This capacity loss is probably due to the above mentioned irreversible electrochemical processes during the first discharge. During the following cycles, good reversible capacity retention and better cycleability were obtained.
was attributed to the formation of SEI film and Ni\textsuperscript{2+} reduc-

ible capacity was observed during the first discharge which obtained for LNTP/C composite even at fast regime. An irre-

versible carbon. Thus, excellent electrochemical performances were

coated Li\textsubscript{0.5}Ni\textsubscript{0.25}TiOPO\textsubscript{4} exhibits smaller particles interconnected

shapes of LNTP/C comparing to the pure oxyphosphate. Carbon

by Raman spectroscopy. SEM pictures show different particle

presence of carbon in the LNTP/C composite was detected only

ing it able to be a host material in the lithium batteries. The

work formed by [TiO\textsubscript{6}] and [NiO\textsubscript{6}] octahedra interconnected by

(\text{S.G. P}\textsubscript{2}1/c). The structure consists of a three-dimensional frame-

formed by [TiO\textsubscript{6}] and [NiO\textsubscript{6}] octahedra interconnected by

many vacancies exist within the structure, making it able to be a host material in the lithium batteries. The presence of carbon in the LNTP/C composite was detected only by Raman spectroscopy. SEM pictures show different particle shapes of LNTP/C comparing to the pure oxyposphate. Carbon coated Li\textsubscript{0.5}Ni\textsubscript{0.25}TiOPO\textsubscript{4} exhibits smaller particles interconnected by carbon. Thus, excellent electrochemical performances were obtained for LNTP/C composite even at fast regime. An irre-

versible capacity was observed during the first discharge which was attributed to the formation of SEI film and Ni\textsuperscript{2+} reduc-
tion. During the subsequent cycles, the Ti\textsuperscript{4+}/Ti\textsuperscript{3+} redox couple is active together with the Ni\textsuperscript{2+}/Ni redox couple during the ele-

trochemical cycling. The capacity retention ranges from 92% to

82% at C/5, C/2 and 1C rates even after 50 cycles. These perfor-

ances are much higher than those obtained for the uncoated Li\textsubscript{0.5}Ni\textsubscript{0.25}TiOPO\textsubscript{4}.

3.5. Conclusion

The carbon coated Li\textsubscript{0.5}Ni\textsubscript{0.25}TiOPO\textsubscript{4} was successfully prepared by using polyethylene glycol as carbon source, under a reducing atmosphere. Rietveld refinement of the X-ray diffraction patterns shows that this oxyposphate exhibits a monoclinic symmetry

(\text{S.G. P}\textsubscript{2}1/c). The structure consists of a three-dimensional fram-

References


The low cycling potential (~1.7 V) and the good capacity reten-
tion during cycling are favourable to consider this oxyposphate rather as a candidate for the negative electrode.

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