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SnHPO₄: a promising precursor for active material as negative electrode in Li-ion cells

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Abstract

SnHPO₄ was synthesized by precipitation and characterized by X-ray diffraction. The discharge curve of electrochemical cells using SnHPO₄ as active cathode material and metallic lithium as anode showed a first reduction step at ca. 1.5 V. X-ray diffraction patterns of lithiated samples showed very weak bands ascribable to metallic tin. For the voltage values lower than 0.8 V the well-known Li–Sn alloy formation takes place. An intermediate step appears in the range from 1.2 to 0.8 V. The capacity retention is stabilized after 10 cycles at ca. 200 mA h/g. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

At present tin-based compounds are intensively studied as negative electrode materials for lithium-ion batteries. This special interest has been developed since the communication by members of the Fuji research laboratories on the outstanding performances of tin-containing glasses [1]. However, a major problem associated to their use results from the formation of large-size metallic-tin clusters during prolonged cycling. Thus, the complete lithium-tin alloying process is hindered, leading to a strong loss of capacity. Tin-based crystalline and glassy oxides have been widely studied, as well as some oxysalts. The presence of atoms indirectly involved in the electrochemical reactions (such as phosphorus or boron), creating a matrix where tin atoms are embedded, seems to have a beneficial effect on the electrochemical performance of these materials. Thus, besides oxides and oxyglasses some tin phosphates were studied such as glassy Sn₂BPO₆ [2], crystalline Sn₂P₂O₇ and SnMn_{0.5}PO₄ [3], Sn₂P₂O₇ [4] and more recently Sn₂PO₄Cl [5]. In this way, we report a preliminary electrochemical study of tin(II) hydrogen phosphate: SnHPO₄.

2. Experimental

The compound SnHPO_4 was obtained by a precipitation procedure. H_3PO_4 (20 ml, 85%) was added to a tin(II) solution (prepared by dissolving 20 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in propylene carbonate (PC) up to 100 ml), with continuous stirring until the precipitation was completed. The precipitate was separated by centrifugation at 10 000 rpm for 10 min, washed several times with absolute ethanol, dried at 60 °C in air for 2 h, and then at 110 °C under vacuum for one day (sample A). Another sample was only dried at 80 °C for one day (sample B). The dissolution of tin chloride in distilled water leads to the precipitation of $\text{Sn}_2\text{PO}_4\text{Cl}$ [5]. X-ray diffraction (XRD) was carried out with a Siemens D5000 diffractometer working with Cu K α radiation and a graphite monochromator.

The electrochemical reactions with lithium were studied in two-electrode cells. The cathode was prepared by mixing the pure compound (70% in weight), poly(tetrafluoro ethylene) PTFE (15%), and carbon-black (15%). The final pellets of 7 mm diameter were obtained by pressing the mixture (10–15 mg) at 250 MPa. The anode consists of a metallic lithium disk. Both electrodes were held in a nickel grid and immersed in the electrolyte (1 M solution of LiPF₆ in ethylene carbonate–dimethyl carbonate (EC:DMC = 1:1). The

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Fig. 1. X-ray diffraction patterns of sample A (top) and sample B (bottom). Rietveld refinement (solid line); experimental (dots) and difference are given for the sample B.



Fig. 2. Projection in the (100) plane of the structure of $SnHPO_4$, showing the double layer of PO_4 units linked by Sn atoms, where the double layers are held together by hydrogen bonding.

galvanostatic discharge-charge curves were obtained at different temperatures, at C/10 (C = 1 Li/mol/h) by

Table 1			
Unit cell	parameters	of	SnHPO ₂



Fig. 3. IR spectra of SnHPO₄, indicating the assignation of the different observed bands. Sample A, solid line; sample B, doted line.

using a multi-channel microprocessor-controlled system (Mac Pile) [6]. The cells were thermostated with water circulation controlled to a temperature of ± 0.05 °C, using a Haake F3K apparatus.

3. Results

3.1. Structural characterization

The X-ray diffraction patterns of the pristine materials shown in Fig. 1 agree well with those reported for SnHPO₄ [7–9]. It has a monoclinic structure, space group $P2_1/c$, with all atoms located in 4e sites. The structure can be described as a double layer of isolated PO₄ tetrahedra, linked by Sn atoms, in the (010) plane, the double layers being held together by hydrogen bonding (Fig. 2). A Rietveld refinement of the data obtained for sample B was carried out to confirm its crystallographic structure. The refined unit cell parameters are included in Table 1.

The IR spectra of both samples were also coincident, as shown in Fig. 3. The normal modes of vibration of a regular PO₄ tetrahedron are: A₁, E (both modes Raman active), and 2 F₂ (Raman and IR active), which are shown in Fig. 3. The PO₄ stretching (PO₄ st) mode appears at ca. 570 cm⁻¹, and the PO₄ bending (PO₄ δ) mode at ca. 1020 cm⁻¹, for free undistorted PO₄ tetra-

	Sample A	Sample B	From Ref. [6]	From Ref. [7]	From Ref. [8]
a (Å)	4.658(1)	4.614(4)	4.576	4.608	4.596
b (Å)	13.667(3)	13.63(1)	13.548	13.603	13.625
c (Å)	5.883(1)	5.834(5)	5.785	5.823	5.824
β (°)	98.77(1)	98.77(1)	98.7	98.8	98.8

hedra. If the T_d symmetry decreases to give C_1 symmetry, each F_2 mode split in 3 A modes, all IR active. Thus, the PO₄ st mode appears as three bands at ca. 580, 555 and 530 cm⁻¹, and the PO₄ δ at 1080, 1025 and 975 cm⁻¹. A similar effect was observed for Sn₂ClPO₄ [5], but in that case the splitting was higher, thus indicating a higher distortion from the theoretical T_d symmetry. Additionally, the presence of the –OH group in HPO₄^{2–} is confirmed by the bands ascribable to O=P–OH bending, PO–H combined, PO–H stretching and OH stretching, as shown in Fig. 3.

3.2. Electrochemical characterization

Fig. 4-top shows the first discharge of the cell using $SnHPO_4$ (samples A and B) as active electrode materials in lithium cells. The first plateau for sample B involves the well-documented reduction of Sn^{II} to metallic Sn, with the theoretical consumption of 2 Li/mol. Concerning sample A, this first plateau extends up to 3 Li/mol. Two Li/mol can be attributed to Sn^{II}/Sn reduction. The third Li/mol cannot be interpreted with similar arguments. No simple explanation



Fig. 4. Cell discharge using SnHPO₄ as the cathode material and metallic Li as the anode material. Top: comparison between samples A and B (the inset shows the evolution of the voltage of the first plateau of sample A as a function of the temperature); middle, derivative curve - dV/dx of the cell discharge curves vs. x; bottom, - dV/dx vs. the voltage.

was found to justify this 1 Li/mol excess consumption. It could be tentatively attributed to a possible H^+ to H_2 reduction, according to:

$$SnHPO_4 + 3 Li \rightarrow Sn + (1/2)H_2 + Li_3PO_4$$

Unfortunately, attempts to extract information from PMR and FTIR spectra of partially lithiated samples were unsuccessful due to the presence of the solvent used to support the electrolyte in cells (the mixture DMC and EC). Especially, in the case of the PMR spectra, a large signal was obtained corresponding to H atoms of solvents, which masks the possible signals of the active phase.

Because a preliminary study showed us that the voltage of the first plateau is highly temperature sensitive, all the results presented here have been carried out under thermostatic conditions. Thus, the voltage of the first plateau varies from 1.49 V at 5 °C to 1.735 V at 40 °C, as shown in the inset of Fig. 4-top). The end of the plateau at ca. 1.5 V is best represented by the derivative curves -dV/dx versus x (Fig. 4-middle). Sample B shows a simple peak at ca. 2 F/Sn (marked B1), corresponding to the end of the Sn^{II} into Sn⁰ reduction, followed by a complex profile. Concerning sample A, the end of the plateau is evidenced by a split peak, centered at ca. 3 F/Sn (marked A1 and A2). On the contrary, the plot of -dV/dx versus V shows similar profiles for both samples (Fig. 4-bottom), with a first peak at ca. 1.3 V (marked A1 and B1, for samples A and B, respectively), and a second peak at ca. 0.9 V (marked A2 and B2). Then, a large band of low amplitude is observed.

3.3. XRD of lithiated samples

The X-ray diffraction patterns of selected partially lithiated samples are shown in Fig. 5a and b. At 2 F/Sn, after the Sn^{II}/Sn⁰ reduction, sample B is completely X-ray amorphous. Very weak bands corresponding to metallic tin are observed. At the same lithiation amount for sample A, the peaks of the pristine product are still visible. It is worth noting that when the sample B reaches the end of the plateau (2 F/mol), for sample A the plateau is still present. Sample A becomes completely amorphous at the end of this plateau, which corresponds to 3 F/mol (ca. 1 V). At the beginning of the initial expected voltage of Li-Sn alloy formation (ca. 0.8 V), the products are always amorphous and metallic tin remains almost undetected by X-ray diffraction. Finally, at the end of the discharge (at 0 V) typical reflections of Li-Sn alloys are absent.

3.4. Cycling results

Fig. 6-top shows the evolution of the capacity during cycling at two different temperatures: 5 and 40 $^{\circ}$ C. In



Fig. 5. (a) X-ray diffraction patterns of selected partially lithiated samples (sample A); reference lines position of Sn and $Li_{22}Sn_5$ are shown. (b) X-ray diffraction patterns of selected partially lithiated samples (sample B); reference lines position of Sn and $Li_{22}Sn_5$ are shown.

both cases, the capacity is almost stabilized after 10 cycles, around 200 mA h/g, being higher for the experiment carried out at higher temperature (ca. 180 mA h/g at 5 °C, 220 mA h/g at 40 °C). For a more prolonged cycling, the relative capacity retention (C_{i+1}/C_i) is practically 100%.

The X-ray diffraction patterns of the active material after 10 cycles are shown in Fig. 6-bottom, where tin reflections are clearly visible. The broadened profiles evidence that the growth of Sn domains took place in a limited extension.

4. Discussion

The Li-Sn alloying process was earlier characterized in the 360-590 °C temperature range [10], which clearly showed the different plateaus and voltage drops in the discharge curve, corresponding to the alloys LiSn, Li₇Sn₃, Li₅Sn₂, Li₁₃Sn₅, Li₇Sn₂ and Li₂₂Sn₅. At room temperature, the Li-Sn alloying process has been described to take place below 0.8 V [11]. The Li_vSn alloys versus Li gives voltages of 0.660 V (0.4 < y <0.7), 0.530 V (0.7 < *y* < 2.33), 0.485 V (2.33 < *y* < 2.63), 0.420 V (2.63 < y < 3.5) and 0.380 V (3.5 < y < 4.4) [12]. Thus, taking into account these previous results, the discharge curve of sample B can be decomposed in three steps. The first step at ca. 1.5 V, which ends at ca. 2 F/Sn (peak marked B1 in the derivative curves), corresponds to the Sn^{II} to Sn⁰ well-known metallic reduction, as observed in other Sn^{II} phosphates [4,5]. The third one, below 0.8 V, is assigned to Li-Sn alloys formation. The second step takes place in the range from 1.2 to 0.8 V (marked B2), which is too low to be Sn^{II}/Sn⁰ reduction, and too high for Li-Sn alloys formation.

Besides, the electrochemical discharge curve of sample A can be interpreted in terms of two steps: the first one corresponds to a reduction of Sn^{II} into Sn^{0} , accompanied by a possible H⁺ reduction, which extends from 0 to ca. 3 F/Sn, according to Fig. 4-top; the second which extends from ca. 3 to 7 F/mol, in the range 0.8–0 V. The capacity reached at this step agrees fairly well



Fig. 6. Top: evolution of the cell capacity as a function of the number of cycles (triangles, at 5 °C; circles, at 40 °C; open, discharge; solid, charge). Bottom: X-ray diffraction pattern of the active material after the 10th cycle.

with the formation of typical Li-Sn alloys. The maximum theoretical capacity is 4.4 Li/Sn, which corresponds to Li₂₂Sn₅. When both samples are compared, a good correspondence is observed in: (a) the process assigned to alloying process (Fig. 4-top); (b) the peaks (A1 and B1, and A2 and B2) in the derivative curves in Fig. 4-bottom. Thus, the first step of the discharge in sample A can be assigned to steps one and two in sample B. While in sample A both processes take place simultaneously, with a single plateau, in sample B these two processes are clearly differentiated. The only evidence of these two processes in sample A appears at the end of the plateau, with a complex voltage drop, which makes appearing two peaks in the derivative curve (marked A1 and A2). Basically, both samples have the same behavior, but the voltage evolution of the two first processes seems to be very sensitive to the way of drying the initial precipitate.

The X-ray diffraction patterns show very weak bands assigned to metallic Sn, while no Li–Sn alloys signals are detected. It implies that metallic tin is highly dispersed in the phosphate matrix, thus large clusters (either metallic tin or Li–Sn alloys) are not formed. This result strongly differs to that observed in other tin phosphates, where reflections were clearly observed at the end of the tin reduction (metallic tin) or/and the end of the discharge (Li–Sn alloys) [4,5]. Since the formation of large metallic-tin clusters during cycling partially prevents the complete lithium–tin alloying process, the absence of these reflections makes this compound an interesting candidate as precursor of active anodic material. After 10 cycles, reflections of metallic tin are visible, indicating that the clusters formation is developed during the successive discharge/ charge cycling. A good design of the cathode pellets would probably hinder this cluster formation, and thus enhance the retention capacity.

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