

## Electrochemical reaction of lithium with $\text{CoP}_3$

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### Abstract

The electrochemical reaction of lithium with the skutterudite-type  $\text{CoP}_3$  compound has been studied. To follow the reaction mechanism, X-ray diffraction (XRD),  $^7\text{Li}$  nuclear magnetic resonance (NMR) and X-ray absorption (XAS) experiments have been carried out. During the first reaction of the  $\text{CoP}_3$  phase, cobalt is reduced and lithium-phosphide is formed. The reversible process observed during subsequent cycles consists of the formation of  $\text{Li}_3\text{P}$  from its elements, giving a maximum in reversible gravimetric capacity of 487 mAh/g. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium; X-ray diffraction; Electrochemical reaction; Cobalt phosphide; X-ray absorption

### 1. Introduction

In the last years, great efforts have been dedicated to study materials that can react reversibly with lithium by means of lithium alloys formation, with the aim of finding alternatives to carbon as anodes in lithium-ion batteries. A large number of these compounds contain either Al, Sb, Sn or Si in their stoichiometries [1]. The electrochemical formation of lithium alloys with these elements avoids the development of dendritic growth of lithium by increasing a few hundred millivolts the potential as referred to the  $\text{Li}^+/\text{Li}$  pair. As shown in early works using the massive metals [2,3], electrode capacities are high resulting from the limit compositions such as  $\text{Li}_{22}\text{Sn}_5$  or  $\text{Li}_3\text{Sb}$ . However, the “electrochemical grinding” induced by marked changes in lattice volume during the charge–discharge cycles leads to the loss of electrical contact between metal particles and a subsequent decrease in capacity. A surprising property of some of these compounds that contain lithium-alloying elements is that the pristine structure can be reversibly modified and reconstructed on electrochemical cycling. This has been demonstrated for  $\text{SnSb}$  [4] and  $\text{Li}_2\text{ZnGe}$  [5].

In recent works, we studied the electrochemical reactions with lithium of antimony-rich compounds, such as the member of the skutterudite family  $\text{CoSb}_3$  [6], the marcasite-related solid  $\text{CrSb}_2$  [7] and the  $\text{TiSb}_2$  compound [8] prepared thermally by direct synthesis. As compared with

massive Sb, the cycling properties of these novel electrode materials are significantly improved. A mechanism that implies the destruction of the compounds with the release of the non-alloying transition metal and the formation of poorly crystalline Li–Sb alloys was proposed. In these materials, the poor crystallinity or even amorphous state of the lithiated electrode makes difficult, a complete characterization of the products by diffraction procedures. Other d-block metals–antimony compounds have also been studied in the literature [9,10].

Together with several antimonide compounds that have been extensively studied due to their thermoelectric properties, the skutterudite-type structure is also presented by  $\text{CoP}_3$ . The low atomic weight and high availability of phosphorous allow us to expect larger gravimetric capacities than antimony-based electrodes and cheaper production. At the same time, the toxicity of  $\text{CoAs}_3$  (skutterudite) is avoided. In this work, we study the reaction of lithium with  $\text{CoP}_3$  in a lithium battery and use X-ray absorption (XAS) to increase the present knowledge about the non-crystalline phases in the reacted electrodes.

### 2. Experimental

$\text{CoP}_3$  was obtained by weighing stoichiometric amounts of Aldrich high purity cobalt and P, grinding them together and enclosing them in a sealed niobium-tube. The tube was slowly heated up to 800 °C for 1 week and quenched to room temperature. X-ray diffraction (XRD) patterns were

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recorded on a Philips diffractometer, using Cu K $\alpha$  radiation equipped with graphite monochromator. For lithiated samples, exposure to air atmosphere was avoided by opening the electrochemical cells inside a dry box and covering the electrodes with a plastic film before recording the ex situ XRD patterns.

For electrochemical experiments, Swagelok-type cells were assembled in a dry box under Ar atmosphere. Negative electrode was Li, and CoP<sub>3</sub> (46%) mixed with carbon (graphite, 46%) and binder (PVDF, 8%) was used as positive electrode. A 1 M solution of LiPF<sub>6</sub> in ethylene carbonate and diethyl carbonate (EC:DEC = 1:1) prepared by Merck was used as electrolyte. Both Whatman glass fiber and Celgard were employed as separators. Galvanostatic charges and discharges were carried out with a MacPile instrument at C/20 rate. This means that 1 mol of lithium reacts with 1 mol of CoP<sub>3</sub> in 20 h.

The XAS experiments at the K edges of Co were performed with the synchrotron radiation of the DCI storage ring at LURE (Orsay, France). The beam line was equipped with a Si(3 1 1) two-crystal monochromator and the resolution was 0.2 eV. The Co–K edge (7709 eV) spectra were recorded (1.85 GeV positrons, average current of 250 mA) in the transmission mode at room temperature. The XAS spectra were normalized to give the same amplitude in the range of atomic absorption. The samples were pellets formed by mixing sample powder and cellulose to have the suitable concentration. <sup>7</sup>Li magic-angle spin (MAS) nuclear magnetic resonance (NMR) spectra were recorded at room temperature on a Bruker ACP-400 spectrometer working at 155.52 MHz resonance frequency and at ca. 4.5 kHz spinning rate. The lithium reference was a 1 M LiCl aqueous solution.

### 3. Results and discussion

The powder XRD patterns of the as-prepared solid (Fig. 1) were consistent with the cubic lattice, Im $\bar{3}$  space group, of the skutterudite-type CoP<sub>3</sub>. The refined unit cell parameter  $a = 7.6694$  Å agrees well with the literature values [11]. Traces of NbP resulting from a partial side reaction with the niobium reactor tube are also visible in Fig. 1.

Fig. 2 shows the first few cycles of a lithium anode cell using CoP<sub>3</sub> as the active material of the positive electrode. During the first discharge, the reaction of Li with CoP<sub>3</sub> takes place mostly in the 0.4–0.25 V potential range through a quasi-plateau, consuming >6 mol of lithium per mol of CoP<sub>3</sub> (ca. 1090 mAh/g). Other experiments were allowed to reach 0 V versus Li during the first discharge, but only a steep fall in voltage was observed <0.25 V with a marked loss of cycling performance, as will be discussed below. Note that the first discharge curve of lithium anode cell using CoSb<sub>3</sub> as active cathode material was characterized by the presence of two plateaus [5]. These two plateaus were attributed to the formation of Li<sub>2</sub>Sb and Li<sub>3</sub>Sb alloys, in agreement with the

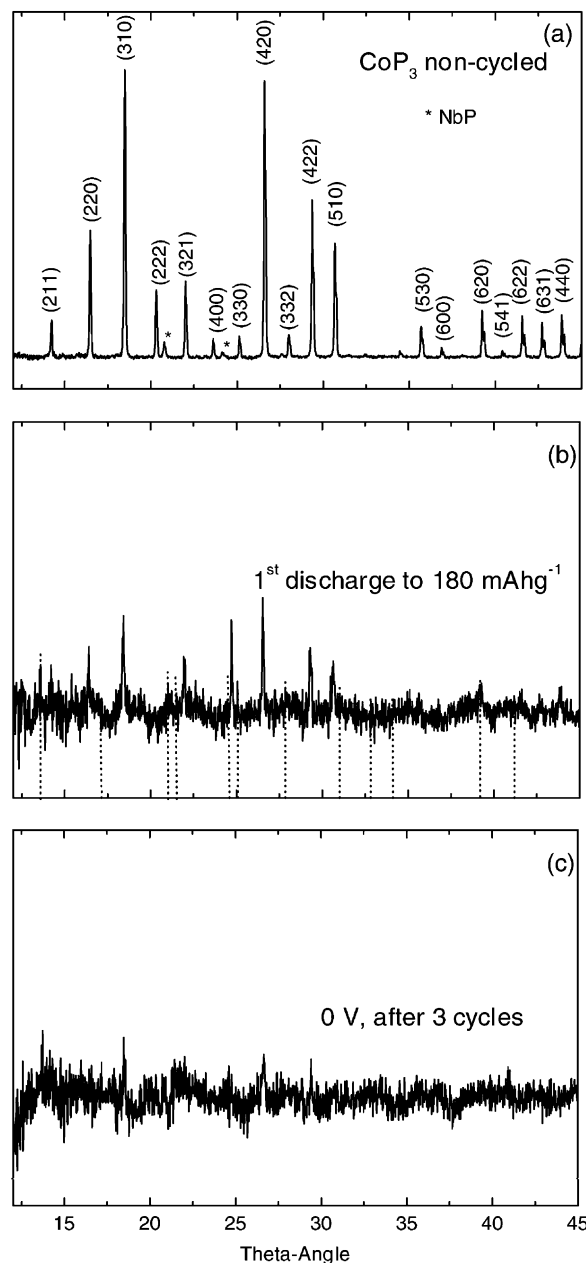


Fig. 1. X-Ray Diffraction pattern of (a) pristine non-cycled CoP<sub>3</sub>, and corresponding electrodes; (b) after first discharge to 180 mAh/g, and (c) at 0 V after 3 cycles. Dashed lines corresponding to the positions of Li<sub>3</sub>P reflections are shown in (b).

previously reported voltage of formation of lithium antimony alloys [1–3]. Contribution of electron consumption due to the formation of a passivating film in the first discharge was also reported [6]. At present, no direct evidence has been reported to support or discard lithium insertion into CoSb<sub>3</sub> during the first steps of the electrochemical reaction. In the case of CoP<sub>3</sub>, the smaller unit cell volume as compared to CoSb<sub>3</sub> makes even less probable a lithium insertion into the skutterudite-type structure.

Having in mind that no Li–Co alloys have been described in the phase diagrams of this system, and the thermodynamically

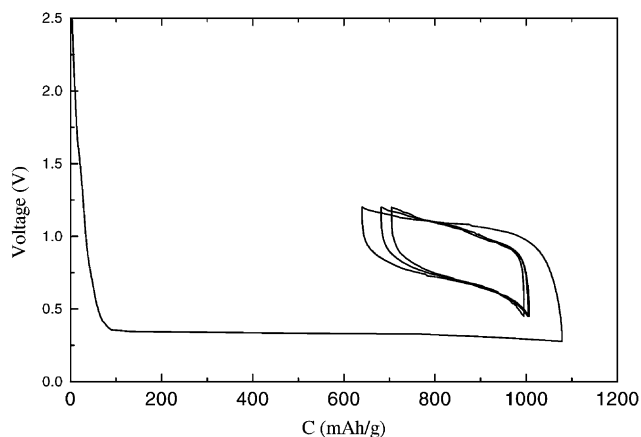
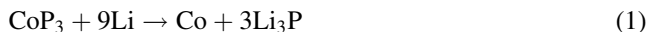


Fig. 2. Electrochemical cycling of Li/LiPF<sub>6</sub>/CoP<sub>3</sub> at C/20 rate. The additives of CoP<sub>3</sub> are 46% graphite and 8% PVDF.

favorable formation of lithium phosphide from the constituent elements, the reaction in which the maximum lithium uptake of the elements is admitted could be:



Ex situ XRD of lithiated electrodes reveal that during reaction with lithium CoP<sub>3</sub> suffers a progressive amorphization. However, the diffraction patterns in Fig. 1 also show the presence of low intensity lines ascribable to lithium phosphide hexagonal phase Li<sub>3</sub>P (P6<sub>3</sub>/mmc space group [12]) marked by dashed lines, which can support reaction (1). No lines reflecting metallic cobalt are visible, presumably because cobalt can be transformed into nanosized particles smaller than the X-ray coherence length. This behavior was also shown in CoSb<sub>3</sub> [6]. Moreover, chromium also remained unidentified in reacted electrodes based on CrSb<sub>2</sub> [7].

Table 1

Edge energies determined from their first derivatives position of XANES spectra.

Sample	Edge energy (eV)
CoP <sub>3</sub>	7710.9
CoP <sub>3</sub> + Li (1st discharge)	7710.4
CoP <sub>3</sub> + 3.9 Li (1st discharge)	7709.7
CoP <sub>3</sub> + 4.8 Li (3rd discharge)	7709.2
Co	7709.2

With the aim of obtaining additional information about the state of cobalt in the discharged electrodes, XANES of the Co–K edge were recorded for the pristine solid and electrodes prepared by interrupting the experiments at several discharge depths (Fig. 3 and Table 1). The XAS spectra at the Co–K edge shows a peak at about 7709 eV. The spectrum reflects the electronic transitions from the Co 1s state to the 4p type empty states. The spectrum scans selectively the Co(4p) empty states showing a very weak peak a but an intense peak b. The spectrum is very similar to the one obtained for CoSb<sub>3</sub> [13], where, from tight binding calculations, the a structure was attributed to Co 3d density of states in the conducting band, and the b structure to the levels issue from hybridization Co(4s, 4p), Sb(5p). High intensity of this second peak showed the strength of the Co–Sb bonds in this structure.

The spectra evidence the progressive displacement of the edge to lower energies on increasing the depth of the discharge, which is indicative of the cobalt reduction process during discharge. The Co metal edge is close in energy to the most lithiated samples. Moreover, the more the samples are lithiated, the less the shape of their XANES is structured.

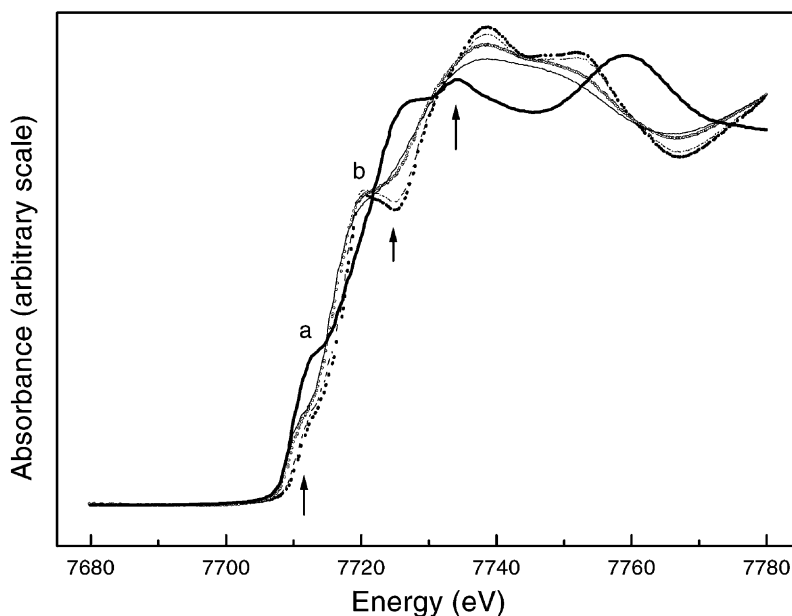


Fig. 3. X-Ray Absorption in Co–K edge of non-cycled CoP<sub>3</sub> (dotted line), after reaction with 1 F/mol of lithium (thin dotted line) and 3.9 F/mol (circles) in the first discharge, and after 3 cycles (4.8 F/mol, in thin solid line). Co (solid line) is shown as reference.

This can be a consequence of the appearance of metal cobalt particles which absorb X-ray at the energy values indicated by arrows in Fig. 3.

On the other hand, the theoretical capacity for reaction (1) is 1620 mAh/g. However, the reversible capacity reached in our lithium cells was always below this value. This behavior contrasts with that found in lithium cells using antimony compounds as the precursor of the lithium alloys [7–9]. In antimony compounds, the occurrence of side reactions with the organic carbonates in the electrolyte solvent leading to the formation of a passivating layer of alkyl carbonates and lithium carbonate was unequivocally shown by vibrational spectroscopy [4,6,8]

Unless the  $\text{CoP}_3$  could be recovered, which is not detected by XRD, the following charge and discharge branches should be associated with the reversible lithium reaction with phosphorus:



Then, the theoretical capacity of 1620 mAh/g could also be expected on further charge and subsequent cycles. However in the experimental second discharge, the lithium cell possesses a reversible capacity of 487 mAh/g, which is still significantly larger than graphite and  $\text{CoSb}_3$ . In order to confirm that reaction (2) is taking place, it should be noted that thermodynamic arguments have been proven efficient in order to evaluate the differences in cell potential between the first and subsequent discharge branches [6,7,9]. While the potential expected for reaction (2) can be simply approached to the free energy of formation of  $\text{Li}_3\text{P}$ , the difference between second discharge and first charge cell potentials can be associated with the free energy of formation of  $\text{CoP}_3$ . Although to our knowledge the  $\Delta G_f^\circ$  value is not found in the literature, the corresponding enthalpy is slightly negative

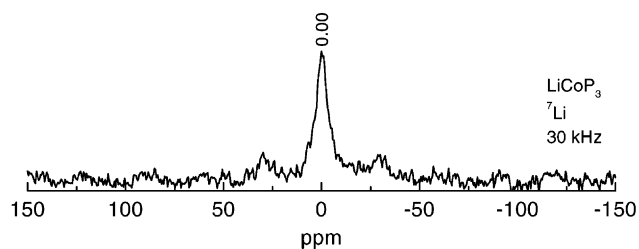


Fig. 4.  $^7\text{Li}$  MAS NMR spectrum of  $\text{CoP}_3$  electrode after reaction with 1 F/mol of lithium.

( $\Delta H_f^\circ = -65$  kcal/mol [14]). However, as crystallinity, and surface properties of both the elements—cobalt and phosphorus—and the lithium alloys are particularly affected, the differences may depart from the simple conversion:

$$\Delta E \text{ (1st - 2nd discharge)} \sim \frac{-\Delta H_f^\circ(\text{CoP}_3)}{F}$$

Additional information concerning the nature of the lithium species in the discharged electrode was obtained by  $^7\text{Li}$  MAS NMR spectroscopy. The experimental spectrum in Fig. 4 shows the presence of a main signal at ca. 0 ppm versus  $\text{LiCl}$ , which is characteristic of an ionic form such as that observed in alkali metal pnictides. It should be noted that the ionicity of the Li–P bonds is high. According to Nazri et al. [15], there is a narrow range of miscibility between  $\text{LiCl}$  and  $\text{Li}_3\text{P}$  and the ionic conductivity of the lithium phosphide chloride revealed a low activation energy for lithium transport.

Finally, the electrochemical performance of lithium cells using  $\text{CoP}_3$  as active material was evaluated in a limited number of cycles. Unfortunately, capacity decays quickly in the successive cycles (Fig. 5). This phenomenon is more marked when the discharge voltage limit is diminished. The

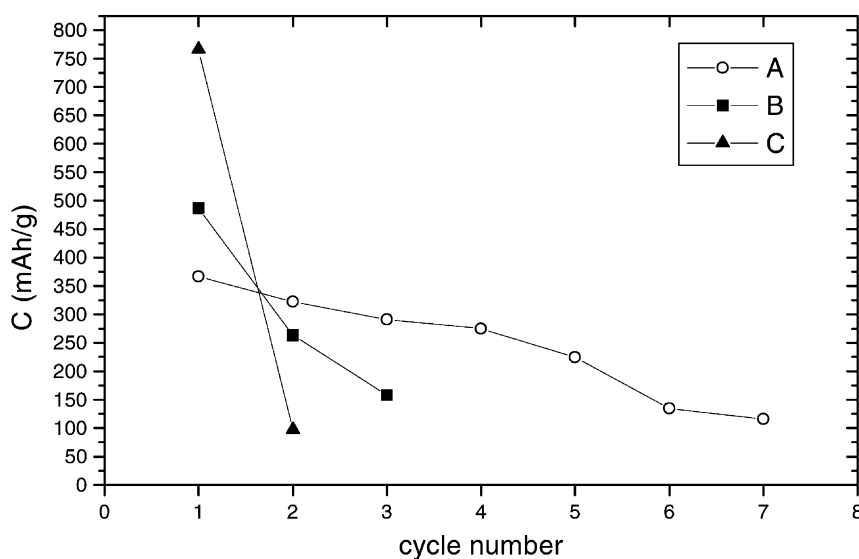


Fig. 5. Evolution of reversible capacity measured in the discharge branch of  $\text{Li/LiPF}_6/\text{CoP}_3$  cells with the first galvanostatic cycles at  $C/20$  rate. Charge voltage limit was 1.2 V. First discharge was stopped after reaction with 6 F/mol of lithium, which corresponds to ca. 1090 mAh/g in the cycle number 0, and the following discharge voltage limits were: (A) 0.45 V; (B) 0.26 V, and (C) 0.1 V.

absence of a passivating layer produced in the first discharge can be the origin of the loss of reversible capacity upon cycling. However, the large value of ca. 600 mAh/g suggests other mechanisms of capacity loss, probably involving isolated particles of P and lithiated material.

#### 4. Conclusions

Lithium reacts electrochemically with  $\text{CoP}_3$  through a single extended quasi-plateau at about 0.4–0.25 V during the first cell discharge. In this process cobalt is reduced as determined by XAS experiments, and an amorphization process takes place. Lithium-phosphide is formed and a part of this lithium can be reversibly extracted by charging, yielding to a reversible capacity of 487 mAh/g in the second discharge.

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