

# CoP<sub>x</sub> synthesis and lithiation by ball-milling for anode materials of lithium ion cells

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## Abstract

Cobalt phosphides and lithiated cobalt phosphides are prepared by high-energy ball-milling at room temperature. With increasing the milling time, the phosphide structure is converted from CoP<sub>3</sub> to CoP phase. The initial electrochemical lithiation of CoP<sub>x</sub> (CoP<sub>3</sub>+CoP) and CoP leads to a reversible capacity of 878 and 533 mAh/g. The faradic yield at the first cycle is about 74% for both the samples. Partial lithiation of the CoP<sub>x</sub> by ball-milling with Li<sub>3</sub>N reactant enhances the initial faradic yield to 95%, along with a sacrifice of part of the reversible capacity. The lithiation by thermoreaction, however, results in poor electrochemical performance.

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## 1. Introduction

Lithium ion battery gets wider and wider application in the world and has become one of the chemical power sources with the most developing potential in the 21st century. To overcome the limitations of low gravimetric and volumetric capacity and safety concerns that commercial carbonaceous anode materials exhibit, intensive study has focused on several new families of electrode materials for lithium ion batteries in recent years. In addition to Sn- and Si-based oxides and intermetallics, an increasing interest is in 3D metal oxides, metal nitrides and phosphides as a possible alternative to carbon materials due to their ability to react reversibly with large amounts of Li per formula unit [1].

Transition metal phosphides, such as MnP<sub>4</sub> [2], CoP<sub>3</sub> [3,4], CuP<sub>2</sub> [5], Cu<sub>3</sub>P [6,7], FeP<sub>2</sub> [8] and Li<sub>2</sub>CuP [9] have been investigated recently as possible candidates for anode

materials in lithium ion batteries. These materials show a large initial gravimetric capacity. Different reaction mechanisms have been proposed depending on the transition metal M as well as the M/P and Li/P ratio in the starting compounds. In MnP<sub>4</sub>, a quasi-topotactic intercalation process is observed. The P–P bonds in the binary layered phosphide are cleaved on reduction to form crystalline Li<sub>7</sub>MnP<sub>4</sub> and reformed on oxidation when MnP<sub>4</sub> is recrystallized [2]. In CoP<sub>3</sub>, the initial uptake of Li forms highly dispersed cobalt clusters embedded in a matrix of Li<sub>3</sub>P, and the extraction of Li on charge yields nanoparticles of LiP [4]. The reaction mechanism of lithium with CuP<sub>2</sub> is different from CoP<sub>3</sub> and MnP<sub>4</sub>. Some new phases of Li<sub>1.75</sub>Cu<sub>1.25</sub>P<sub>2</sub> and Li<sub>2</sub>CuP form during the reaction [5]. On the other hand, FeP<sub>2</sub> uptakes six lithium atoms to form amorphous Li<sub>6</sub>FeP<sub>2</sub> [8].

Cycling of MnP<sub>4</sub> and CoP<sub>3</sub> involves a conversion between two phases: providing a large theoretic capacity and presenting a single potential plateau for charging or discharging, which is favorable for a stable voltage output of the related cell. In this study, we adopt convenient but efficient high-energy ball-milling techniques to synthesize cobalt phosphides and the lithiated cobalt phosphides for

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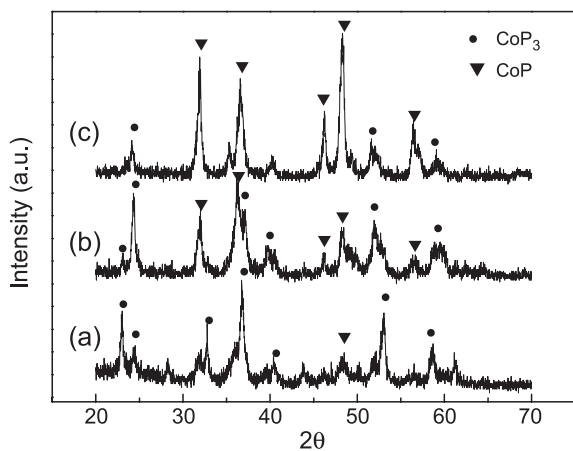


Fig. 1. XRD patterns of  $\text{CoP}_3$  obtained with different milling time. (a) 10 h, (b) 15 h, defined as sample A, (c) 20 h, defined as sample B.

anode materials of lithium ion cells. Their charging and discharging properties are investigated.

## 2. Experimental

Planetary Mono Mill P-6 (Fritsch, Germany) was used for the synthesis of cobalt phosphides. The starting materials were stoichiometric mixtures of cobalt powder (200 mesh) and red phosphorus. In an Ar-filled glove box, a total of ca. 2.5 g powder mixture was loaded into a hardened steel bowl with 80 ml volume, together with 15 hardened steel balls in 10 mm diameter. The bowl was sealed and then moved to the outside of glove box. Ball-milling was conducted at a speed of 500 rpm. There was a 15-min pause after each 1-h milling. The total milling time was controlled. After ball-milling, the samples were heated until 500 °C under Ar atmosphere to remove remnant phosphorus. Partially lithiated cobalt phosphide was prepared by ball-milling stoichiometric amounts of  $\text{Li}_3\text{N}$  powder and the synthesized phosphide sample. The milling time was 5 h at a speed of 500 rpm. High-temperature lithiation was performed by pressing the same precursor mixture into a pellet and heating at 400 or 500 °C in vacuum or in Ar gas.

X-ray diffraction (XRD) patterns were recorded with an automated powder diffractometer, using the  $\text{Cu K}\alpha$  radiation (type: D-max 2550 V). For the XRD measurement of lithiated samples, a polyethylene (PE) protection film was used to prevent it from contacting air.

For electrode fabrication, cobalt phosphide powder was mixed with acetylene black (10%) as electron conductor and PVDF (8%) dissolved in NMP as binder. The slurry was spread on the foamed nickel disc (14 mm in diameter), followed by drying and pressing processes. The electrode containing lithiated active material was prepared in Ar-filled glove box, using PTFE as binder. CR2016-type coin cells with the test electrode, 1 M  $\text{LiPF}_6/\text{EC}+\text{DMC}$  (1:1 in volume) electrolyte and lithium counter electrode were assembled to evaluate the electrochemical cycling perform-

ance of cobalt phosphide samples. Charge (lithiation) and discharge (delithiation) was performed at a constant current density of 0.3  $\text{mA}/\text{cm}^2$  with controlled voltage cutoff.

## 3. Results and discussion

High-crystalline  $\text{CoP}_3$  has been synthesized by high-temperature method in a sealing condition. After electrochemical lithiation, the material structure turns to be quasi-amorphous [3,4]. Our interest here is to prepare low-crystalline and fine-granular cobalt phosphides by high-energy ball-milling and to study their electrochemical behavior. Fig. 1 shows XRD patterns of the samples prepared with the same precursor composition but different milling time. The remnant phosphorus in the samples has been removed by heat-treatment at 500 °C (sublimating point of red phosphorus: 427 °C) before the structure analysis. Broad peak width and weak diffraction intensity suggest that the crystallinity of the samples is poor. With increasing the milling time, the product structure changes from  $\text{CoP}_3$  to CoP phase.  $\text{CoP}_3$  is the main component below 11 h, and CoP becomes dominant above 20 h. In the meanwhile, a mixture ( $\text{CoP}_3+\text{CoP}$ ) is obtained. However, it should be mentioned that the CoP phase was not found in the product obtained by high-temperature reaction. In addition, this intermediate phase was also not detected when lithium was electrochemically inserted into  $\text{CoP}_3$  [3,4]. It means that a reaction that followed “ $2\text{Li}+\text{CoP}_3\rightarrow\text{CoP}+2\text{LiP}$ ” does not occur there.

The initial three cycle profiles of sample A ( $\text{CoP}_3+\text{CoP}$ ) and sample B (mainly CoP) are exhibited in Fig. 2. The first lithiation capacity is, respectively, 1180 and 724 mAh/g for samples A and B. The charge efficiency is about 74%, slightly different from each other. If CoP reacts with lithium to form nanosized Co like  $\text{CoP}_3$  [lithiation:  $\text{CoP}+3\text{Li}^++3\text{e}^-\rightarrow\text{Li}_3\text{P}+\text{Co}$ , delithiation:  $\text{Li}_3\text{P}\rightarrow\text{LiP}+2\text{Li}^++2\text{e}^-$ ], the

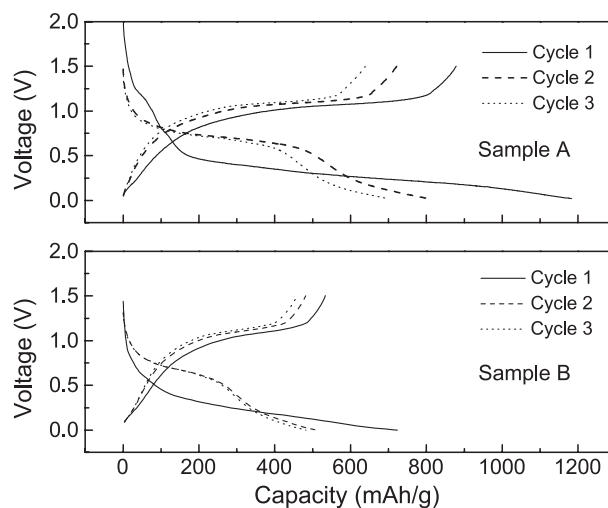


Fig. 2. The initial three cycle profiles of samples A and B, voltage cutoff: 0.02/1.5 V.

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