Short communication

Cobalt phosphide as a new anode material for sodium storage

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HIGHLIGHTS

- CoP nanocrystals are synthesized by a facile ball-milling method.
- CoP electrode delivers a high specific capacity of 770 mAh g^{-1}.
- The sodium storage mechanism of CoP is investigated by ex-situ XPS and STEM.

ARTICLE INFO

ABSTRACT

A novel anode material for sodium ion batteries - nanosized CoP particles - was synthesized by a facile and productive ball-milling method. The CoP was tested as an anode candidate for sodium ion batteries. It delivered a high initial specific capacity of 770 mAh g^{-1}, and excellent rate capability, demonstrating that CoP is a promising anode candidate for sodium ion storage. *Ex-situ* X-ray photoelectron spectroscopy and scanning transmission electron microscopy were carried out to investigate the sodium storage mechanism of CoP.

1. Introduction

Nowadays, sodium ion batteries (SIBs) are considered as the most promising substitute for lithium ion batteries (LIBs) in energy storage systems, and have been drawing more and more attention from electrochemical researchers [1–10]. This is because the price of sodium is much lower than that of lithium due to the abundance of sodium reserves. For sodium ion batteries, however, the most important issue that needs to be addressed is the development of good electrode materials with excellent cycling performance and superior specific capacity. In the case of the anode materials, the elements which can alloy with sodium are currently being intensively investigated, owing to the high theoretical capacity that they can deliver in SIBs, including Sn (847 mAh g^{-1}) [11], Sb (664 mAh g^{-1}) [12], and P (2596 mAh g^{-1}) [13–15]. Among these elements, phosphorus is a particularly high-profile research subject. The big disadvantage of phosphorus, however, is the huge

volume changes (490%) during the sodiation/desodiation, resulting in pulverization of the electrode material accompanied by poor cycling performance [14].

Generally, there are three ways to overcome the poor cycling performance. The first is to synthesize nanosized materials [16–19]. It is very difficult, however, to use a chemical method to prepare nanosized P. In a previous report, even though the particles were nanosized, the cycling performance was still unstable, due to the poor electronic conductivity of P. Thus, this method to synthesize nanosized structures is not suitable for P. The second way is to coat a conductive and elastic layer on the surface of the active material to form a composite, which can not only improve the electronic conductivity, but also act as a buffer to absorb the stress from the volume expansion. Recently, some papers have reported P/carbon composites, such as P/Super P [13,15], P/carbon nanotubes (CNTs) [14], P/graphene [20], etc. The results show that the cycling stability of P was improved dramatically. The third way is to prepare an alloy compound, which has been confirmed as an effective method to overcome the disadvantages resulting from huge volume expansion in both LIBs and SIBs [21–25]. Qian et al. reported that Sn$_4$P$_3$/C composite showed significantly better cycling performance than

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that of P/C composite, with 86% capacity retention after 150 cycles [26]. Kim et al. reported that Sn_4P_3 compound without any introduction of carbon exhibited negligible capacity fading over 100 cycles [27]. Moreover, the $Sn_{4+x}P_3$@amorphous (Sn–P) composite prepared by our group also exhibited excellent cycling stability, with 92.6% retention of the second cycle capacity over 100 cycles [28]. Accordingly, forming an alloy compound is an effective way to improve the cycling performance of P.

In this work, cobalt phosphide (CoP) compound was prepared on a large scale by a facile ball-milling method. In this sample, the metal (Co) is inactive and acts as a conductive matrix to buffer the volume expansion. Then, CoP as a new anode material was tested in sodium half-cells. CoP electrode can deliver a high reversible capacity of more than 700 mAh g^{-1}, which offers a new alternative to carbonaceous anode materials in Na cells. Cobalt phosphide (CoP) would be a promising anode for sodium ion storage.

2. Experimental section

2.1. Synthesis of CoP phosphide

Co (>99.8%, Sigma) and red P (>99%, Sigma) was used as the starting materials without further purification. CoP was prepared by the simple ball-milling method using the corresponding stoichiometric molar ratio of the metal (Co) to P. The starting materials were put into a hardened steel vial with milling balls 2 mm in diameter. The weight ratio of milling balls to powder was 20:1. The vial was assembled in an argon-filled glove-box and then mounted on the ball mill machine (Pulverisette 7, Fritsch). The vial is so airtight that it can keep the Ar atmosphere during the milling process. The rotation speed of the mill was set to 300 rpm for 20 h.

2.2. Characterization

The crystalline structure of the active powder was characterized by powder X-ray diffraction (XRD) on a GBC MMA diffractometer with a Cu K_α source. The morphology of the sample was investigated by field emission scanning electron microscopy (FESEM; JEOL JSM-7500FA) and transmission electron microscopy (TEM, JEOL 2011, 200 keV). The sodium storage mechanism of CoP was determined by scanning transmission electron microscopy (STEM, JEOL ARM200F) equipped with energy-dispersive X-ray spectroscopy (EDS), and X-ray photoelectron (XPS) was conducted using a SPECS PHOIBOS 100 Analyzer installed in a high-vacuum chamber with the base pressure below 10^{-8} mbar.

2.3. Electrochemical measurements

The CoP electrodes were prepared by mixing 70% active materials, 10% carbon black, and 20% carboxymethyl cellulose (CMC, which is water soluble) binder by weight to form an electrode slurry, which then was coated on copper foil, followed by drying in a vacuum oven overnight at 80 °C, and then pressing at 30 MPa. The electrodes were punched into round disks with 3 mg cm^{-2} loading of active material, and then the electrodes were kept in the glovebox. The sodium foil was cut by the doctor blade technique from a sodium bulk stored in mineral oil, which then was employed as both reference and counter electrode. The electrolyte was 1.0 mol/L $NaClO_4$ in an ethylene carbonate (EC) - diethyl carbonate (DEC) solution (1:1 v/v), with or without 5 vol.% addition of fluoroethylene carbonate (FEC). The cells were assembled in an argon-filled glove box. The cycling performances were tested on a Land Test System at current density of 100 mA g^{-1} in the voltage range of 0–1.5 V (vs. Na$^+$/Na). The rate capability of the CoP electrode was tested at the current density from 100 to 2000 mA g^{-1} in the

voltage range of 0–1.5 V (vs. Na$^+$/Na), and the electrode is charged for 5 cycles at each current density.

3. Results and discussion

The structure and morphology of CoP were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Fig. 1(a) shows the XRD pattern of the CoP. From the XRD pattern of the as-obtained CoP, the intensity of the CoP peaks is very low, and the peaks are very broad, indicating that the particle size is very small. The CoP phase was indexed to orthorhombic phase with Pnma space group (JPCDS No. 29-0497, a = 0.5077 nm, b = 0.3281 nm, c = 0.5587 nm). Moreover, the SEM and TEM images of CoP also demonstrate that the CoP particles are very small (Fig. 1(b and c)). As shown in Fig. 1(c), the morphology of the as-prepared CoP mainly presents amorphous characteristics, with small crystals 10–20 nm in size embedded in the amorphous matrix. The d-spacings of these CoP nanoparticles are 0.254 nm and 0.283 nm, assigned to the (200) and (011) planes, respectively. The selected area electron diffraction patterns (SAED) are indexed to the orthorhombic phase, and the diffraction rings correspond to the (020), (211), (200), (011), and (201) planes, as shown in Fig. 1(d). It is worthy noticing that the as-prepared CoP is not sensitive to air, however, if it is kept under air for long time, it will be oxidized. Thus, it is kept in glove boxes. To detect the component of the amorphous part in the TEM image, energy-dispersive X-ray spectroscopy (EDS) mapping is carried out, and the results are shown in Fig. 1(e). As shown in Fig. 1(e), it is clear that the amorphous matrix mainly consists of amorphous P and small amount of Co.

The electrochemical performance of CoP as anode for sodium ion batteries was tested within the voltage window of 0–1.5 V. The electrolyte was 1 M $NaClO_4$ in a solution of EC:DEC = 1:1, (v/v). Fig. 2(a) shows the charge/discharge curves of the CoP electrode at the current density of 100 mA g^{-1}. During the first discharge, the CoP electrode features one sloping profile in the voltage range of 1.0–0.5 V, which corresponds to the solid electrolyte interphase (SEI) film formation due to the electrolyte decomposition and the irreversible conversion reaction of CoP. Additionally, there is one obvious potential plateau at 0.05 V, which is similar to that of P assigned to the formation of Na_3P [13–15]. The charge–discharge curves of CoP in SIBs are similar to those of iron phosphide (FeP) in SIBs [29], suggesting that they have a similar storage mechanism, i.e., the P in the CoP is alloyed with Na to form Na_3P. The equation is listed as follows:

$$CoP + 3Na^+ + 3e^- \rightarrow Co + Na_3P \tag{1}$$

Moreover, the CoP electrode delivered 770 mAh g^{-1} initial discharge capacity with 65.2% initial coulombic efficiency, which is close to the theoretical capacity of 893.3 mAh g^{-1} for Na_3P formation (Fig. 2(a)). The reason for the lower than theoretical capacity is the pulverization caused by the low electronic conductivity of the SEI film. To clearly show the voltage plateau, the dQ/dV curves are plotted in Fig. 2(b). It is clear that there are two couples represented by the reversible peaks at 0.05/0.46 V and 0.21/0.58 V in the second cycle dQ/dV curves, as shown in Fig. 2(b). The peaks at 0.21/0.58 V are ascribed to the Na_xP (Na_2P, NaP and NaP_7) intermediate phase formation/decomposition, while the ones at 0.05/0.46 V correspond to the Na_3P formation/decomposition [13]. Thus, the sodium storage mechanism of CoP anode can be explained as a reaction between Na and the P resulting from the decomposition of CoP.

Fig. 2(c) shows the cycling performance of CoP electrodes in sodium ion batteries. In the second cycle, the CoP electrode