



## Enhanced capacity of chemically bonded phosphorus/carbon composite as an anode material for potassium-ion batteries



Xuan Wu<sup>a</sup>, Wei Zhao<sup>b</sup>, Hong Wang<sup>a</sup>, Xiujun Qi<sup>a</sup>, Zheng Xing<sup>a</sup>, Quanchao Zhuang<sup>a,\*\*</sup>, Zhicheng Ju<sup>a,\*</sup>

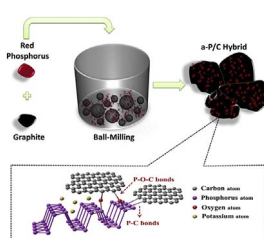
<sup>a</sup> School of Materials Science and Engineering, China University of Mining and Technology, Xuzhou, Jiangsu 221116, PR China

<sup>b</sup> School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou, Jiangsu 221116, PR China

### HIGHLIGHTS

- Phosphorus/Carbon composite is prepared by mechanical ball-milling.
- Red P transforms into stable amorphous black P be observed.
- Stable phosphorus-carbon bond alleviates the volume expansion.
- The mechanism of phosphorus is proposed to form a KP phase.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Potassium-ion batteries are attracting great attention as a promising alternative to lithium-ion batteries due to the abundance and low price of potassium. Herein, the phosphorus/carbon composite, obtained by a simple ball-milling of 20 wt% commercial red phosphorus and 80 wt% graphite, is studied as a novel anode for potassium-ion batteries. Considering the high theoretical specific capacity of phosphorus and formation of stable phosphorus-carbon bond, which can alleviate the volume expansion efficiently, the phosphorus/carbon composite exhibits a high charge capacity of  $323.5 \text{ mA h g}^{-1}$  after 50 cycles at a current density of  $50 \text{ mA g}^{-1}$  with moderate rate capability and cycling stability. By the X-ray diffraction analysis, the alloying–dealloying mechanism of phosphorus is proposed to form a KP phase. Meanwhile, prepotassium treatment is conducted to improve the low initial coulomb efficiency.

### 1. Introduction

Requirement for Li-ion batteries (LIBs) is promptly increasing in powering electronic devices and vehicles [1,2]. However, the rising price resulted from the shortage and uneven geographical distribution of Li resource cause a worry about the heavy dependence on LIBs [3,4]. Hence, more investigative attention has been paid to other replaceable technologies, such as Sodium-ion batteries (SIBs) and Potassium-ion batteries (PIBs) [5,6]. Compared with 0.0017 wt % of lithium, sodium and potassium element take up 2.3 wt % and 1.5 wt % respectively in

the earthcrust [7]. In the past decade, a lot of progress has been made on the development of SIBs [8,9]. However, relatively limited study has been concentrated on PIBs.

Considering the lower negative redox potential of  $\text{K}/\text{K}^+$  ( $-2.93 \text{ V}$ ) compared with  $\text{Na}/\text{Na}^+$  ( $-2.71 \text{ V}$  for), the working voltage of PIBs is higher than that of SIBs, allowing PIBs to operate at higher potentials and improving energy density [10–12]. Therefore, the PIBs are very promising alternative candidates for Electrical Energy Storage (EES). The cathodes of PIBs have made some progress, where Prussian blue/Prussian blue analogues [13] and  $\text{FeSO}_4\text{F}$  [14] show excellent capacity

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [zhuangquanchao@126.com](mailto:zhuangquanchao@126.com) (Q. Zhuang), [jucz@cumt.edu.cn](mailto:jucz@cumt.edu.cn) (Z. Ju).

and cycling performance. Nevertheless, investigation on the anode of PIBs remains a breakthrough. Graphite, as a commercial LIBs anode, only forms  $\text{NaC}_{64}$ , merely showing an inferior capacity of  $\sim 35 \text{ mA h g}^{-1}$  but can form  $\text{KC}_8$  with a remarkable capacity of up to  $\sim 273 \text{ mA h g}^{-1}$  [15–20]. Although the capacity is not very high and fades quickly, it still provides many new ideas toward rechargeable PIBs.

From an electrochemical perspective, phosphorus with a fairly light atomic quality and large Li-uptake and Na-uptake ability ( $\text{Li}_3\text{P}$ ,  $2596 \text{ mA h g}^{-1}$ ;  $\text{Na}_3\text{P}$ ,  $2596 \text{ mA h g}^{-1}$ ), can also be used in PIBs with a high theoretical capacity of  $2596 \text{ mA h g}^{-1}$  by forming  $\text{K}_3\text{P}$ , according to the binary phase of K-P [21–24]. Phosphorus elemental has three allotropes of white phosphorus, red phosphorus and black phosphorus. White phosphorus cannot be used as an anode due to its toxic and chemically unstable character. Red phosphorus with a low electronic conductivity of  $1 \times 10^{-10} \text{ S cm}^{-1}$  could reduce electrochemical redox reactions although it has an abundant reserve and low cost. Black phosphorus has higher electron mobility than red phosphorus. As a new kind of 2D semiconductor material, it is the thermodynamically and chemically most stable one among them and could be an ideal anode material [25,26]. Furthermore, to restrain the inherent volume expansion of phosphorus during the charge and discharge process, several methods have been often employed, such as amorphousizing active phases and dispersing the phosphorus element in a buffering matrix [27,28]. Of course, it is also crucial and effective to keep good electric connection between P and the matrix and finally form chemically stable bond, which could be frequently caused by ball milling [29], radio frequency plasma deposition [30] and chemical vapor deposition [31,32]. Among them, mechanical ball milling could be the simplest one. For example, Sultana et al. obtain pure black phosphorus encapsulated into a carbon matrix by ball milling, showing a much higher capacity in PIBs. Meanwhile, based on the alloying mechanism to yield a KP alloy as the final phase, dramatic volume change can also be restricted by controlling the potential range [33]. Moreover, Zhang and co-workers also successfully introduce the superior  $\text{Sn}_4\text{P}_3/\text{C}$  composite by a conventional and scalable ball-milling technique, which shows a superior electrochemical performance in PIBs [21]. These investigations contribute to the search for a safe, high-energy-density, and low-cost rechargeable PIBs in the large-scale energy storage applications.

Hence, to solve the above issues, phosphorus/carbon composite (P/C) is synthesized by a simple mechanical ball-milling of 20 wt% commercial red phosphorus and 80 wt% graphite under an Ar atmosphere lasting for 48h. The schematic diagram is shown in Fig. 1 and the detailed experimental steps are given below. As we all known, large particles can be crushed down to smaller size and layered materials can be exfoliated by shear stress during the ball milling. In this study, the bulk red phosphorus is grinded to smaller particles, shortening the potassium-ion transport path and alleviating particle breakage resulted from volume expansion of phosphorus during potassiation. Meanwhile, combining the high specific capacity of amorphous phosphorus and the uniform distribution of carbon matrix which can not only effectively relieve the volume expansion, but also exhibit potassium storage capacity to some extent, the as-prepared P/C composite shows a high capacity, moderate cycling stability and rate performance, indicating that it could be a promising anode for PIBs.

## 2. Experimental section

### 2.1. Materials and synthetic procedure

Phosphorus red ( $\text{P}_4$ ,  $\geq 98.5\%$ , Aladdin, China) and graphite powder ( $\text{C}$ ,  $\geq 99.8\%$ , Aladdin, China) are used directly without further purification. In a typical synthetic process, the phosphorus/carbon composite (P/C) is obtained by direct ball milling of red phosphorus and graphite with a mass ratio of 20:80. The weighed raw powders are blended and then placed into a steel mill pot together with the mass

ratio of milling balls to reagent powders of 20:1. Then, the milling pot is put into the glove box filled with argon, sealed by Teflon tape and set in a planetary ball miller (QM-35P2, Nanjing, China). The rotation speed of the miller is set to 500 rpm for 48 h. The compared composite with different mass ratio of phosphorus and carbon is also obtained in the same condition.

### 2.2. Physical structure characterization

X-ray diffraction (XRD) analysis is performed with a Bruker D8 advanced X-ray diffractometer equipped with Cu  $\text{K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Diffraction data is collected by step scanning over an angular range of  $10\text{--}70^\circ$  or slow step scanning in  $20\text{--}40^\circ$ . Scanning electron microscope (SEM, Hitachi, SU8220) and transmission electron microscopy (JEOL JEM-1200EX and ARM-200F field-emission TEM) are used to investigate the morphology and size of the samples. X-ray photoelectron spectroscopy (XPS) is used to observe the valence states and distribution of elements by using Kratos XSAM800. Raman spectra are characterized by a Raman spectrometer (Renishaw 1000B, 532 nm laser excitation). The fully discharged or charged P/C samples are handled carefully to avoid exposing to air. To be specific, the samples are firstly cleaned in DMC solution in the argon-filled glove box and then put into a carefully sealed glass bottle. These samples that are carefully protected from air are used to conduct XRD tests.

### 2.3. Electrode fabrication and electrochemical measurements

The electrodes are obtained by mixing the P/C composite, Sodium Carboxymethyl Batteryulose (CMCNa, M.W. 90000, Aladdin, China) and carbon black (C, AR, Aladdin, China) in deionized water, with a mass percentage of 70:20:10 in a ball-milling process for 4 h. The well-spread solution is distributed on a clean copper foil and placed into the oven at  $80^\circ\text{C}$  for 8h. Then it is punched into a round electrode. The batteries are assembled in the size of 2032 by the separator of glass fibre (GF/D, Whatman) and K foil (K, 99.5%, Aladdin, China) as the counter electrode. The electrolyte is 0.8 M potassium hexafluorophosphate ( $\text{KPF}_6$ ,  $\geq 98.0\%$ , Aladdin, China) dissolved in ethylene carbonate (EC, 99.0%, Sigma-Aldrich, USA) and diethyl carbonate (DEC, 99.0%, Sigma-Aldrich, USA) at a volume ratio of 1:1. The concentrations of water in the electrolyte are tested by automatic trace moisture meter (TPWSC, DT-305) to maintain below 10 ppm. All the preparation processes are in an argon-filled glove box (Mikrouna, Super 1200/750), where the concentrations of moisture and oxygen are maintained below 1 ppm. The galvanostatic and rate charge/discharge performance are conducted by LANHE CT2001A (LAND, P. R. China) and the cyclic voltammetry (CV) measurements are tested by electrochemical workstation CHI660D (LK-2005A, Tianjin, China).

## 3. Results and discussion

### 3.1. Composition and structure characterization

The XRD of the as-obtained P/C composite is displayed in Fig. 2. Fig. 2a is the diffraction peaks of pristine graphite with an intense diffraction peaks located at  $2\theta = 26.2^\circ$ , indexed to the (002) plane (PDF no. 75–1621), showing a high crystallinity. Red P is amorphous, with two obvious broad humps at  $15\text{--}25$  and  $30\text{--}40^\circ$  in Fig. 2b. In Fig. 2c, the P/C composite exhibits a novel diffraction pattern, totally unlike that of red phosphorus and crystalline graphite. Similar diffraction patterns for phosphorus/carbon composite synthesized by ball milling for a long time are reported previously, indicating a structural transformation from red P into black P due to the impact of high temperature and high pressure in the ball-milling conditions [28,34]. When the ball-milling continues for longer time, the structural of generated black P will collapse gradually, finally resulting in an amorphous characteristic. Such a phase transformation from red P to a stable amorphous black P can

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