

Electronic Supplementary Information (ESI)

Reversible 3-Li Storage Reactions of Amorphous Phosphorus as High Capacity and Cycling Stable Anodes for Li-ion Batteries

Jiangfeng Qian^a, Dan Qiao^a, Yuliang Cao^{b*}, Xinping Ai^b and Hanxi Yang^{a*}

^a College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China.

^b Hubei Key Laboratory of Electrochemical Power Sources, Wuhan University, Wuhan 430072, China.

Corresponding author: E-mail: hxyang@whu.edu.cn

1. Experimental details

Materials preparation. The amorphous phosphorus/carbon composite was prepared by direct ball milling of red phosphorus powders (99.3% purity) and Super P carbon (TIMCAL Graphite & Carbon) in an optimized mass ratio of 7:3. The starting materials were weighed, mixed and then put into a steel vial together with 10 mm milling balls. The weight ratio of milling balls to reagent powders was selected to be 20:1. The milling vial was filled with Ar and set in a shaking miller (QM-3A, Nanjing, China). The rotation speed of the miller was set to 1200 rpm for 24 h.

Structural and electrochemical characterizations. The crystalline structure of the active powder was characterized by powder X-ray diffractometry (XRD) on a Shimadzu XRD-6000 diffractometer with CuK α source. The size and morphological view of the powder were observed by Scanning Electron Microscopy (Sirion 2000, FEI) and Transmission Electron Microscopy (JEM-2010HT and JEM-2010FEF). Micro-Raman spectra were collected on a RM-1000 Renishaw Confocal Raman Microspectroscopy with 514.5 nm laser radiation at a laser power of 4mw in the range of 150 to 2000 cm⁻¹.

The electrochemical measurements of the amorphous phosphorus/carbon as anode-active materials were examined by 2032 type coin cells. The working electrode were made by coating an electrode slurry containing 80 wt % active material, 10 wt% CMC binder and 10 wt% conductive carbon (Super P) on copper foil substrate. Then the electrode film was dried in 60 °C oven for overnight. The mass loading of the active material within the film was about 3 mg cm⁻². Lithium foil served as the counter and reference electrode. The electrolyte was 1 mol L⁻¹ LiPF₆ dissolved in a mixed solvent of ethylene carbonate (EC) - dimethyl carbonate (DMC) - ethylene methyl carbonate (EMC) - fluo ethylene carbonate (FEC) (Guotai-Huarong Co., China). The capacity of the material was calculated on the mass of phosphorus, not including carbon content. All the cells were assembled in a glove box with water/oxygen content lower than 1 ppm and tested at room temperature. The galvanostatic charge/discharge test was conducted on LAND cyler (Wuhan Kingnuo Electronic Co., China). Cyclic voltammetric measurements were carried out with coin cell at a scan rate of 0.02 mV s⁻¹ using a CHI 660a electrochemical workstation (ChenHua Instruments Co., China).

2. Morphological and structural characterization of the amorphous phosphorus-carbon composite (a-P/C):

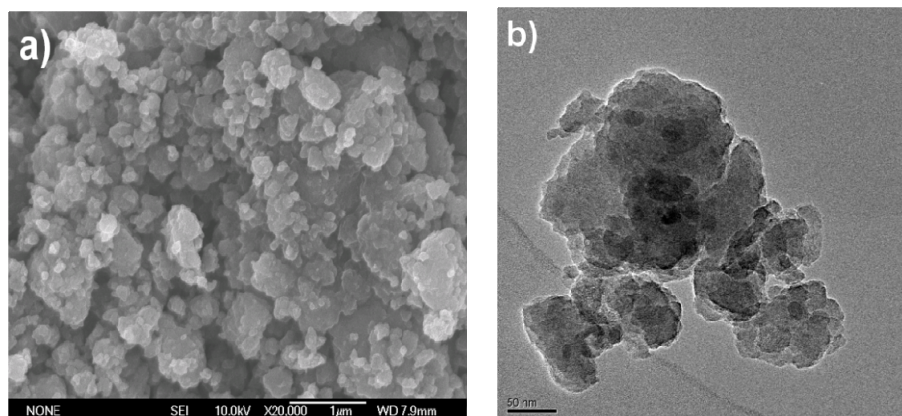


Figure S1. a). SEM and b). TEM images of the amorphous phosphorus-carbon composite.

3. Raman spectra of the P/C composites ball-milled at different milling time

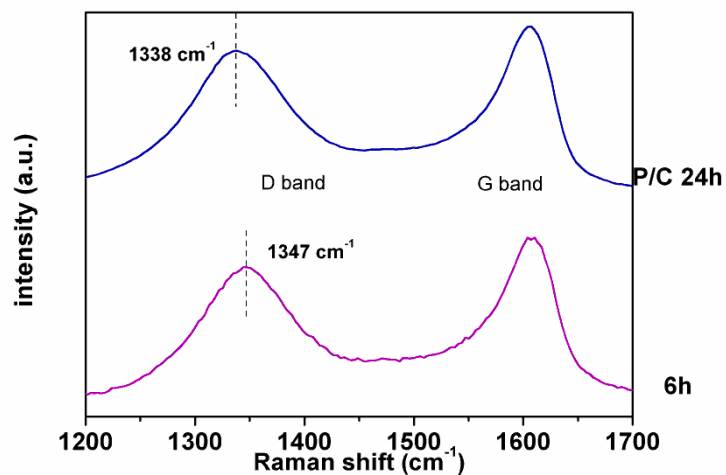


Figure S2. Raman vibration modes for the carbon in the P/C composites ball milled for different time.

4. Cycling performances of the P/C composites ball-milled for different periods

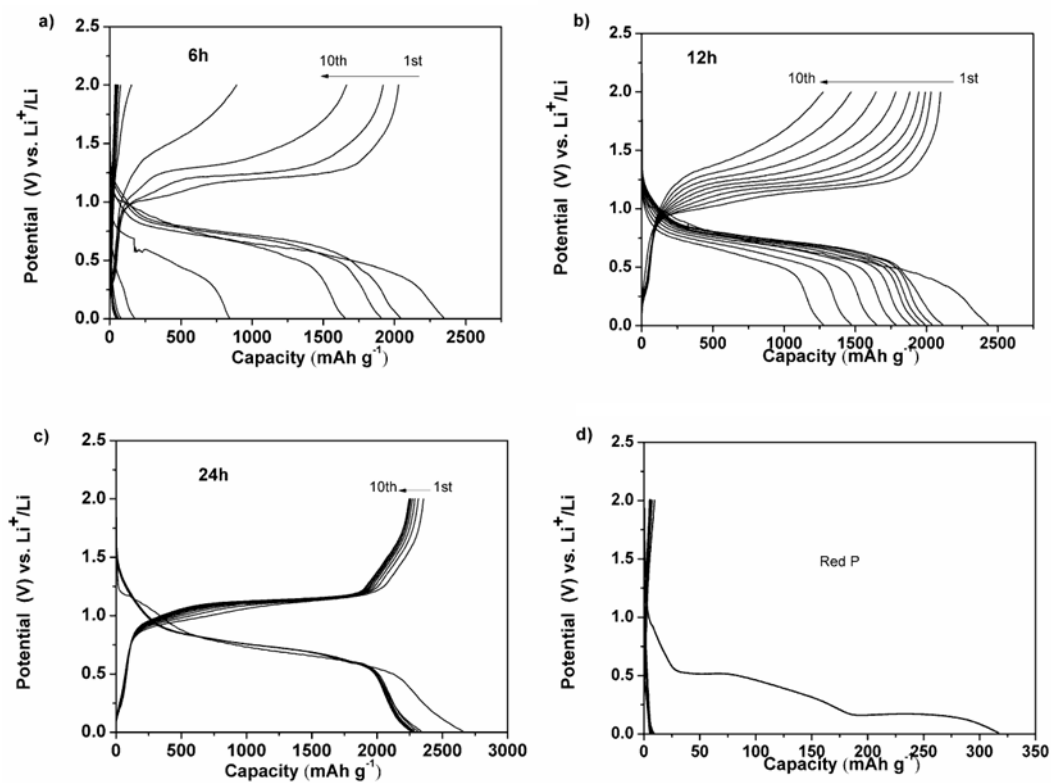


Figure S3. a)-c). Charge-discharge profiles of the P/C composite ball-milled for different periods of 6 h, 12 h and 24 h, respectively; d). Charge-discharge profiles of commercial red P; The electrodes were cycled at a constant current of 250 mA g^{-1} .

5. XRD patterns of the a-P/C anode charged at different depths.

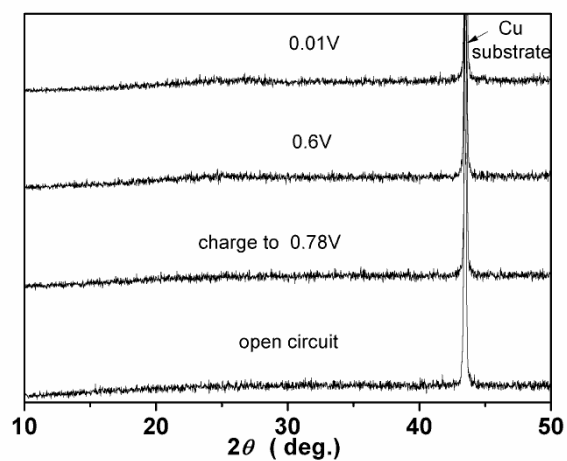


Figure S4. XRD patterns of the a-P/C anode charged to different depths from open circuit to 0.78V, 0.6V, and 0.01V.

Ex situ XRD analysis of the a-P/C electrode at different depths showed a complete amorphous feature across the whole voltage range of 0-2V without any distinct peaks of Li_xP intermediate phases.

6. X-ray photoelectron spectra of the a-P/C composite.

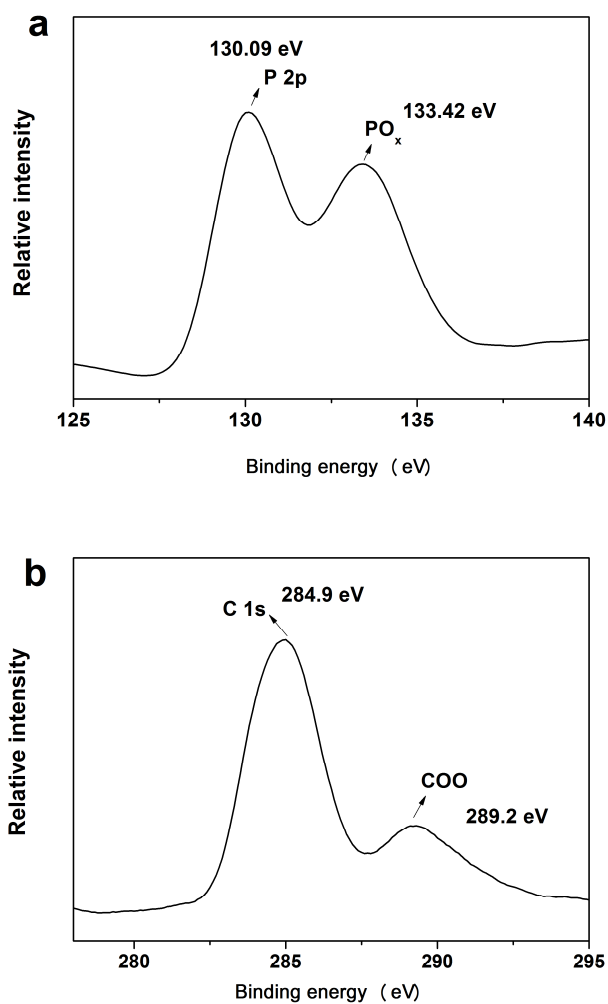


Figure S5. X-ray photoelectron spectra of the a-P/C composite electrode a) P2p signals; b) C1s signals.

7. BET surface areas of the P/C composites ball-milled for 6 h, 12 h and 24 h.

Table S1. BET surface areas of the P/C composites ball milled for different times

samples	BET surface areas
6 h	8.06 m ² /g
12 h	9.47 m ² /g
24 h	10.30 m ² /g

The BET surface areas of the P/C composites ball-milled for 6 h, 12 h and 24 h are 8.06 m²/g, 9.47 m²/g and 10.3 m²/g, respectively. Correspondingly, the initial capacity increases from 2028 mAh g⁻¹ to 2098 mAh g⁻¹ and to 2355 mAh g⁻¹ for 6 h, 12 h and 24 h -milled samples. With increasing milling time from 6h to 12h and then to 24h, the P particles became smaller and then well-dispersed in the carbon matrix, producing a large electrochemically favorable surface for Li insertion reaction.