



Enhanced reversibility of red phosphorus/active carbon composite as anode for lithium ion batteries



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ARTICLE INFO

Article history:

Received 4 December 2014
Received in revised form 3 February 2015
Accepted 17 February 2015
Available online 18 February 2015

Keywords:

Red phosphorus
Active carbon,
Reversibility
Anode materials
Lithium-ion batteries

ABSTRACT

An advanced anode material for lithium ion batteries, amorphous red phosphorous/active carbon composite (P/AC) with a high P content of 60.0 (wt.%), is prepared via a vaporization adsorption method. In the composite, amorphous red phosphorous is mainly loaded into the micropores of the AC matrix. The P/AC composite delivers an excellent capacity up to about 1550 mAh g⁻¹ that is calculated on the basis of composite weight. The high capacity means that approximate 3 electrons are involved in the electrode reaction. At the same time, the P/AC composite exhibits a good cyclability with a capacity retention ratio of 83.6% after 50 cycles. Furthermore, the coulombic efficiency maintains above 97.5% in all the cycles except for the first cycle (76.1%). During the initial cycle, the lithiated and delithiated P/AC anode are further investigated. The formation of SEI film in the initial active process is confirmed. The high and stable electrochemical performance of P/AC composite benefits from the nanoscale of active mass P particles and its homogeneous dispersion onto the conductive AC substrate.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) have been widely applied to many fields due to their high energy density and long cycle life [1–5]. In recent years, the development of hybrid electric vehicles (HEVs) and electric vehicles (EVs) has demanded LIBs with higher energy density [6–8]. The typical Li-de/intercalation compounds in the commercial rechargeable LIBs such as LiCoO₂, LiFePO₄ and graphite are facing huge challenge to meet the needs [9–12]. Some novel electrode materials with outstanding energy density are attracting more and more attention such as sulfur cathode (Li₂S, 1675 mAh g⁻¹) and silicon anode (Li_{4.4}Si, 4200 mAh g⁻¹) [13–17]. For the anode materials, the low lithiation potential is helpful to improve the energy density of batteries. However, a too low lithiation potential would decrease the safety of batteries because of the dendrite of Li metal on the surface of anode [18]. Red phosphorus as one of the promising anode materials with a huge theoretical specific capacity of 2596 mAh g⁻¹ (Li₃P) and a suitable lithiation potential (0.75 V), are increasingly studied in a couple of years [19–25]. Due to its low electric conductivity (<10⁻¹⁴ S cm⁻¹) the pure commercial red P exhibits very low charge/discharge capacity and rapid capacity fade [19–21,26]. In most recent reports,

carbon materials as excellent conductive substrates are introduced to red P anode such as conductive carbon black, activated carbon, mesoporous carbon and carbon nanotubes via a hand-grinding, a ball-milling method or a vaporization-condensation method [20–25]. Basically, the higher P content involved in P/C composite, the lower cyclic capacity and the worse reversibility are observed [22]. Moreover, the used carbon substrates have obvious effect on the final electrochemical performance [22–25], which can be attributed to different dispersion state of amorphous P in carbon substrates. Herein, a commercial activate carbon (AC) with a huge specific surface (1805 m² g⁻¹) and a high micropores volume (0.884 cm³ g⁻¹) (see Table 1) is utilized as conductive substrate to load red P via a vaporization-adsorption method at 500 °C for 4 h followed by 300 °C for 20 h. The homogeneous-dispersed P/AC composite presents excellent cyclic capacity and good electrochemical reversibility.

2. Experimental

2.1. Synthesis and structural characterization of composite

The red phosphorus/active carbon composite was synthesized via a vaporization adsorption method [23]. The commercial activate carbon (TF-01, Tianfu Co. China), with good conductivity and excellent absorbability, was used to prepare the phosphorus/carbon composite. The commercial red phosphorus (0.4 g, 98.9%,

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Table 1
Surface area and pore-structure parameters of AC substrate and red P/AC composite.

Samples	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	V (cm^3/g)	
		$V_{\text{meso}}^{\text{b}}$	$V_{\text{micro}}^{\text{c}}$
Blank AC	1805	0.458	0.884
Red P/AC	453	0.446	0.026
Subtracted value ^d	1352	0.012	0.858

^a BET surface area.

^b BJH desorption cumulative volume of pores between 1.70–300.00 nm.

^c HK adsorption cumulative volume of micropores.

^d The reductive value of surface area and pore volume between the blank AC and the red P/AC composite.

100 mesh, Alfa Aesar) was put in the bottom of a ceramic crucible (50 ml) and AC (0.1 g) was spread on the upside down crucible lid, then were heated to 500 °C for 4 h followed by 300 °C for 20 h in a sealed stainless steel (SS) vessel filled with Ar. The thermal treatment temperature at 500 °C is higher than that in Ref [22,23,25] to promote the faster diffusion of P vapor. Moreover the extra thermal treatment at 300 °C is beneficial to the transformation from white P gas into red P solid ($\Delta_r G_m = -253.6 \text{ kJ mol}^{-1}$ at 300 °C). The P amount in the as-prepared composite was less than the initial amount due to inevitable P loss during the process. The as-prepared P/AC composite was washed with anhydrous ethanol and deionized water for several times to eliminate impurities and then dried at 60 °C for 24 h in a vacuum oven. The phosphorus content in the as-prepared composite was confirmed by TGA (Mettler Toledo, TGA/DSC1) under Ar atmosphere with a flow rate of 50 mL min⁻¹ at a heating rate of 10 °C min⁻¹ from 30 to 800 °C. The microstructure and morphology of the samples were confirmed using XRD (Rigaku MiniFlex II), SEM (Hitachi S-4800) and TEM (FEI Tecnai F20). The Brunauer, Emmett and Taylor (BET) surface areas and pore size distribution were obtained from nitrogen adsorption/desorption curves with a Beijing JWGB JW-BK122 W Micropore Analyzer.

2.2. Battery Assembly and Electrochemical measurements

The as-prepared P/AC composite was mixed with acetylene black (AB) and polytetrafluoroethylene (PTFE) in a weight ratio of 70:20:10 with ethanol as a dispersant. The mixture was spread into a thin piece on a stainless steel plate with a roller, and then was cut into a round film disk with a diameter of 8 mm and a typical weight

of 2.5 mg. The anode film disk was dried at 50 °C for 12 h before assembling the testing cells. The test cells were assembled in a glove box under the Ar atmosphere with lithium metal as a counter and reference electrode, microporous membrane (Cellgard 2300) as a separator and copper foil as a current collector for both anode and cathode. The electrolyte (Jinniu, China) was composed of LiPF₆ (1 M) in a mixed solvent of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1, by volume). Galvanostatic charge/discharge tests were carried out (Land CT2001C, China) at the current density of 140 mA g⁻¹ at ambient temperature. The cut-off potential range for the charge/discharge processes was between 0.05 and 2.0 V (Vs. Li/Li⁺). Both the electrochemical capacity and cycle stability of the electrode were based on the weight of the whole composite. Cyclic voltammograms (CVs) were carried out with an electrochemical workstation (LK2005, China) at a scan rate of 0.1 mV s⁻¹ within the voltage range of 0.05–2.0 V.

3. Result and discussion

3.1. Structure of the as-prepared red P/AC composite

Fig. 1a shows X-ray diffraction (XRD) spectra of the as-prepared red P/active carbon composite, red P and active carbon. All the XRD diffraction peaks of the as-prepared composite can be indexed to red P, and no signals of black P and white P are observed [27–30]. The wide peaks located at 15.5° and 34.1° are indexed to the amorphous structure of red P. Similarly, the commercial AC shows an amorphous structure with wide peaks at the low angle region. The content of red P in the composite is measured by thermogravimetry analysis (TG) in Fig. 1b. The curve shows only one sharp weight loss peak at 400–450 °C, corresponding to the sublimation of red P. The accurate content of red P in the P/AC composite is 60.0%.

The scanning electron microscopy (SEM) images and the energy dispersive X-ray spectroscopy (EDX) analysis are shown in Fig. 2(a–d). The as-prepared P/AC composite and AC substrate have a similar morphology in which micrometer-sized particles are aggregated. After loaded red P, the sharp edges of active carbon seem much smoother due to a layer of red P adsorption on the surface. The inset of Fig. 2c shows the EDX analysis of the P/AC composite, demonstrating the presence of P element. Fig. 2d exhibits the EDX mapping of P and C elements in the P/AC composite, showing the homogeneous dispersion of element P in the AC substrate. Fig. 2e and f show the mesopore and micropore distribution of the as-

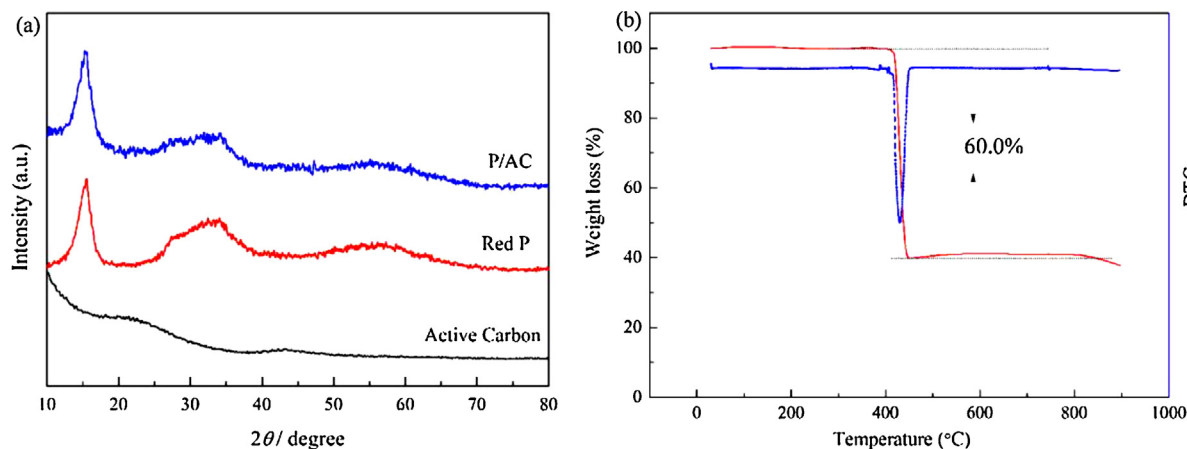


Fig. 1. (a) X-ray diffraction spectra of the as-prepared red P/AC composite, red P and AC. (b) TG and dTG curves of the as-prepared P/AC composite under Ar.

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