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3D red phosphorus/sheared CNT sponge for high performance lithium-ion battery anodes

Tao Yuan[a,b,1], Jiafeng Ruan[a,b,1], Chengxin Peng[a,b], Hao Sun[a,b], Yuepeng Pang[a,b], Junhe Yang[a,b], Zi-Feng Ma[c], Shiyou Zheng[a,b,*]

[a] *School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China*
[b] *Shanghai Innovation Institute for Materials, Shanghai 200444, China*
[c] *Shanghai Electrochemical Energy Devices Research Center, Department of Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China*

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ABSTRACT

Phosphorus (P) is considered one of the most attractive anodic materials for lithium-ion batteries (LIBs) owing to its high theoretical specific capacity (2596 mAh g^{-1}). Nevertheless, it suffers from intrinsic poor conductivity (10^{-12} S m^{-1}) and large volume expansion (~440%) during the lithiation process, leading to low reaction dynamics and serious capacity decay upon cycling. In this work, red P confined in a three-dimensional (3D) sheared carbon nanotube (SCNT) conductive sponge is prepared, showing high capacity and long cyclability as anodes for LIBs. The resultant 3D P-SCNT composite delivers a stable capacity of 1600 mAh g^{-1} at a current density of 0.1 A g^{-1} and a reversible high-rate capacity as high as 782 mAh g^{-1} at 2 A g^{-1} even after 3000 cycles, owing to the robust support of the SCNT framework and stable chemical bonds between the evenly distributed red P and SCNT.

1. Introduction

Phosphorus (P) has been considered one of the most promising activity anode materials for next-generation lithium-ion batteries (LIBs) due to is small atomic weight, large Li-storage ability (Li_3P, 2596 mAh g^{-1}) and much safer operating potential during lithiation (ca. 0.7 V vs. Li/Li^+) than the commercial graphite anode [1,2]. However, the insulating intrinsic nature (electronic conductivity < 10^{-14} S cm^{-1}) for the P anode and its large volume change during lithiation (ca. 440%) result in a large initial irreversible capacity loss and poor cyclability [3]. To address these issues, alternative material-tailoring approaches have been employed, including reducing the particle size of P to shorten the ion diffusion paths and fabricating conductive matrix-confined P composites to enhance the conductivity and maintain the intimate contact between phosphorus and the conducting matrix [4].

Various carbon-based materials, such as one-dimensional (1D) carbon nanotubes (CNTs) [2,4], two-dimensional (2D) graphene [1,5] and 3D carbon aerogels [6,7], have been used to combine the commercial P particles, to improve the electrical conductivity of the P anode and accommodate volume changes of P during lithiation/delithiation as well. Despite some encouraging advancements, there are still severe issues that hinder the electrochemical performance of P-based materials. For instance, poor electrical contact and an uneven distribution of P ascribed to the simple hand-grinding or high-energy ball-milling of P/carbon materials result in rapid capacity decay [4,8]. Moreover, Zhu et al. demonstrated that a vaporization-condensation process in vacuum and at high temperature was advantageous for the diffusion of P vapor into the empty spaces within the tangled CNTs bundles, ensuring sufficient dispersion of red P [9]. Although CNTs possess a high average Young's modulus and large average tensile strength, the discontinuous CNT bundles may not be an ideal carbon host because of its inconsistent electronic conduction in the P-C composite. Carbon aerogel, as a novel 3D interconnected architecture, is regarded as an ideal electrode structure for both electron and ion transfer during cycling. Gao et al. fabricated a 3D red C@P/graphene aerogel composite. The P particles were confined in the graphene aerogel structure to accommodate the volume expansion of red P during cycling [6]. Pei et al. reported 3D P nanoparticles encapsulated in a graphene scrolls structure to restrain the volume change of P [7].

In contrast to the conventional graphene aerogel, herein, we fabricated a novel 3D integrated red P/sheared CNT composite (P-SCNT) via an advanced hydrothermal self-assembly and vaporization-condensation method to achieve a uniform distribution of P nanopar-

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[*] Corresponding author at: School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China.
E-mail address: syzheng@usst.edu.cn (S. Zheng).

[1] These authors contributed equally to this work.

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ticles within the 3D sheared CNT-based architecture. The novel 3D sheared CNT aerogel sponge possesses intrinsically coupled units with 1D single- or few-wall CNTs inside and a 2D sheared mono carbon layer outside. The unique structure acts as a multidimensional electronic conduction system with a high specific surface area and high porosity coupled with the characteristics of hardness and flexibility, which can effectively improve the conductivity of the P and buffer the structural strain/stress caused by the large volume change during lithiation/delithiation process. The as-prepared P-SCNT electrode delivers ultrahigh capacities of 1600 mAh g^{-1} (based on the composite) at 100 mA g^{-1} and stable high-rate capacity as high as 807 mAh g^{-1} at 2 A g^{-1} even after 2000 cycles. This integrated 3D P-SCNT material, with a high reversible capacity, high rate capability and stable cycling performance, could be used as a promising anode for LIBs.

2. Materials and methods

2.1. Synthesis of SCNT sponge

The SCNT sponge was synthesized from multiwall carbon nanotubes (MWCNTs) (purity: > 95%, with average length of 10 µm and average diameter of 11 nm, purchased from Cnano Technology, Ltd.) by a modified Hummers' method [10,11]. The purchased pristine MWCNTs were first purified by calcination at 600 °C for 1 h and washed repeatedly with HCl/HNO_3 to eliminate any metallic impurities for the following experiments.

The processed MWCNTs were oxidized first to grow oxidized functional group on their outer walls. The concrete procedures are as follows: first the processed MWCNTs (5 g) were mixed with concentrated sulfuric acid (150 mL) in a flask. After stirring for 10 min in an ice bath, sodium nitrate (3.5 g) was added into the mixture slowly and stirred for another 10 min. Then, potassium permanganate (20 g) was continuously added into the mixture slowly and stirred for 5 h at 40 °C. Subsequently, the mixture was diluted by 300 mL deionized water. After stirring for 45 min, another 450 mL of deionized water together with 50 mL of 30% H_2O_2 were added to the mixture. After standing for at least 12 h, the resulting mixture was centrifuged and dialyzed to remove the inorganic acid and the impurities. Before transferring to the hydrothermal reactor, the oxidized MWCNT suspension was concentrated to 10 mg mL^{-1} and ultrasonicated for 30 min.

The concentrated oxidized MWCNT suspension (15 mL) was fed into a 20 mL reagent bottle, and the bottle was placed into a 100 mL Teflon-lined stainless steel autoclave for hydrothermal self-assembly at 180 °C for 24 h. During the hydrothermal process, the outer walls of the MWCNTs were unzipped by deoxidation. Simultaneously, the SCNT hydrogel with robust mechanical behavior was self-assembled. The as-prepared SCNT hydrogel was freeze-dried for the following synthesis.

2.2. Synthesis of P-SCNT composite

The P-SCNT composite was prepared by the infiltration of red P powder (98.5%, Aladdin) into the SCNT sponge precursor (mass ratios of m_{SCNT}:m_P=1:1) at 700 °C calcination for 4 h in an evacuated quartz capsule. The as-prepared P-SCNT composite was collected and washed with a CS_2 solution no fewer than three times to remove the residual white P generated during the condensation process. For comparison, the pristine SCNT sponge without P was annealed at the same procedure and then mixed with equal amounts of P powder by mechanical grinding. The obtained hybrid P and SCNT mixture was designated P/SCNT.

2.3. Physical characterizations

The morphology and microstructure of the samples were characterized by an FEI Nova SEM 230 equipped with an ultra-high-resolution field-emission scanning electron microscope (FE-SEM) (INCA X-Max 80, Oxford Instruments) and a transmission electron microscope (TEM) (JEM-2100F, JEOL, Ltd., Japan). Porosity and Brunauer-Emmett-Teller (BET) surface areas for the samples were measured using a nitrogen sorption instrument (Micromeritics, ASAP2020). The X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-2200/PC X-ray diffractometer at 40 kV and 20 mA, with a Cu Kα radiation in the 2-Theta range from 10 to 80°. The Raman spectroscopies of the samples were obtained in dispersive Raman microscope (Senterra R200-L, Germany). Fourier transform infra-red (FTIR) spectra were recorded on a Bruker 22 spectrometer in the frequency range of 4000–500 cm^{-1}. The surface properties of the samples were analyzed by X-ray photoelectron spectrometer (XPS, Kratos Axis Ultra DLD).

2.4. Electrochemical measurements

Electrochemical analyses were carried out using 2032-type coin cells for a half-cell system at room temperature (approximately 25 °C). The active electrodes were prepared using a slurry containing 85 wt % active material, 8 wt % carbon black, and 7 wt % polyvinylidene fluoride (PVDF). The slurry was coated on the current collector of copper foil. The amount of active material loaded on the electrode was about 0.8 mg cm^{-2}. The electrodes were cut into round pieces with a diameter of 1.2 cm by a precision disc cutter machine, and then dried in a vacuum oven at 100 °C for 24 h before being transferred to the glovebox. The coin cells were assembled in the glovebox with lithium metal as the counter and reference electrodes, a microporous polypropylene Celgard 3501 (Celgard, LLC Corp., USA) as a separator, and 1 M $LiPF_6$/EC/DMC (1:1 by volume ratio) as the electrolyte.

The charge and discharge performances were tested at various rates in the potential range of 0.01–3.0 V vs Li/Li^+ using a LAND CT2001A model battery test system (Wuhan Jinnuo Electronics, Ltd.) under constant current conditions. The cyclic voltammetry (CV) tests were performed over the potential range of 0.01–3.0 V using a Gamry Reference 6000 (Gamry Co., USA) at a scan rate of 0.1 mV s^{-1}. The current densities and specific capacities of P-SCNT electrodes are calculated based on the mass of the P-SCNT composite.

3. Results and discussion

3.1. Structural and morphological features

The procedure of the 3D P-SCNT is schematically shown in Fig. 1. First, the pristine MWCNTs undergo a pre-oxidization process, introducing abundant oxidative functional groups and defects on the outer walls of each MWCNT (Fig. 1**a**). Owing to these functional groups, the oxidized-MWCNTs can disperse uniformly in the water. Next, the above oxidized-MWCNTs are hydrothermally self-assembled at 180 °C over 24 h, forming a black hydrogel of 3D SCNT (Fig. 1**b**). During the hydrothermal reaction, the oxidative functional groups on the outer wall of the MWCNTs are reduced under high temperature and pressure [12]. At the same time, the C-C bonds in the outer walls of the MWCNTs, which connected with oxidative functional groups, are broken. Thus, the outer walls of MWCNTs are unzipped to become mono carbon layers, which enwrapped the inner CNTs to become an intrinsically coupled structure. After freeze-drying (Fig. 1**c**), the as-obtained 3D SCNT sponges presents an interconnected porous structure, with pore size distributions from 2 to 100 nm, indicating a large number of mesopores and macropores within the sponges (Figure S1a). This kind of porous structure facilitates the absorption of P vapor into the SCNT host by the capillary effect during the subsequent vaporization process (Fig. 1**d**). After vaporization at a high temperature of 700 °C, a large driving force was created for the P vapor to easily diffuse into the empty spaces of the SCNT host [9]. The BET specific surface area was reduced from 310.9 m^2 g^{-1} of the pristine SCNT to 24.8 m^2 g^{-1} of the P-SCNT composite (Figure S1b), and the pore volume was