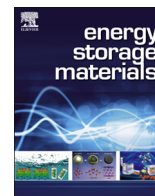




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Carbothermic reduction synthesis of red phosphorus-filled 3D carbon material as a high-capacity anode for sodium ion batteries

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ABSTRACT

Phosphorus is an attractive negative electrode material for sodium ion batteries due to its high theoretical specific capacity of 2596 mA h g^{-1} . However, it suffers poor conductivity ($10^{-12} \text{ S m}^{-1}$), slow reaction dynamics, and large volume expansion ($\sim 440\%$) during the sodiation process, leading to rapid capacity decay upon cycling. Great attention has been devoted to improving the electrical conductivity via mixing phosphorus particles with conductive carbon materials, yet little emphasis has been placed on addressing the volume expansion issue, which may lead to the loss of electrical contact between the active material and the current collector, and the subsequent deterioration of the overall electrochemical performance. Here, we demonstrate a carbothermic reduction method to fabricate ultrafine red phosphorus particles ($\sim 10 \text{ nm}$) embedded in a three-dimensional carbon framework, in which numerous interconnected nanopores are generated accompanied by the carbonization of polyethylene glycol. During discharge/charge processes, nanosized phosphorus particles accommodate the large stress without cracking, and decrease the diffusion length, as well as connect strongly with carbon framework, resulting in an improved conductivity, a reversible specific capacity of 1027 mA h g^{-1} (at 0.2 C) and high capacity retention of 88% over 160 cycles.

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1. Introduction

Growing energy needs and depletion of fossil-fuel resources demand the pursuit of sustainable energy alternatives, including both renewable energy sources and sustainable storage technologies. Therefore, it is essential to consider material abundance, eco-friendly synthetic processes and performance when designing new electrochemical storage systems. Sodium ion batteries (SIBs) have recently received a lot of attention as a low-cost and environmentally friendly alternative to lithium ion batteries (LIBs), [1–3] due to the ready availability of sodium resources and the similar chemistry of sodium and lithium ions [4,5]. Although SIB and LIB share many technical similarities in cathodes and electrolytes, [6–8] adapting LIB anode materials to SIBs has revealed an unsuccessful strategy. The representative example is the Li–Si alloy anode, which can store 4.4 Li per Si, and deliver a specific capacity

of 4200 mA h g^{-1} [9]. However, Si cannot be electrochemically sodiated, in spite of the existence of Na–Si alloys [10]. Moreover, it is also difficult to find crystalline host anode materials for Na-ion insertion reaction partially because of the large diameter of Na (2.04 \AA) compared to Li (1.52 \AA). For example, Na ions cannot be intercalated into the two-dimensional layered graphite [11].

Phosphorus (P) electrochemically reacts with Na to form Na_3P , and delivers a theoretical specific capacity of 2596 mA h g^{-1} , [12] which is much higher than other anode candidates, such as germanium ($\text{Na}_{15}\text{Ge}_4$, 369 mA h g^{-1}), [13] tin ($\text{Na}_{15}\text{Sn}_4$, 847 mA h g^{-1}), [14] lead ($\text{Na}_{15}\text{Pb}_4$, 485 mA h g^{-1}), [15] and antimony (Na_3Sb , 660 mA h g^{-1}) [16]. Moreover, red P is earth-abundant and non-toxic. However, it is synthesized industrially starting from the toxic and very reactive white P, it suffers from a poor electrical conductivity ($10^{-12} \text{ S m}^{-1}$) [17] and has a large volume expansion ($\sim 440\%$) during the sodiation process, leading to rapid capacity decay upon cycling. To improve the electrical conductivity, commercial phosphorus particles have been mixed with various carbon materials, [18–24] such as, carbon black, [19–21] carbon nanotubes and [22,23] grapheme [24]. However, there is little success on

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solving the other problem i.e. the large volume expansion upon sodiation, similarly as Si anode for LIBs, [25,26] which leads to the loss of electrical contact of active materials and deterioration of the electrochemical performance upon cycling.

In order to simultaneously solve the problems of the poor conductivity, large volume expansion and harmful synthesis process, herein, we demonstrate a synthesis strategy of carbothermic reduction of P_4O_{10} into P, resulting in embedding red P nanoparticles in a three-dimensional (3D) carbon framework (P/C composite). Such a design has multiple advantages: (1) The resulting, ultrafine red P particles, with a diameter of ~ 10 nm, not only minimize the diffusion distance of sodium ions, but also allow for a favorable accommodation of the large volume changes without the fracturing that can occur in bulk or micron-sized materials. (2) Red P particles are electrically connected to the conductive 3D carbon framework via P–O–C bonds: the carbon framework functions as an electrical highway and a mechanical backbone, so that all the red P particles are electrochemically active. (3) The interlinked channels are easily filled with electrolyte, thus facilitating the transportation of a large flux of Na ions. (4) A scalable and bottom-up method is applied to fabricate the designed structure, by which P_4O_{10} is the substitute for the toxic white P.

2. Materials and methods

2.1. Synthesis of P/C composite

P_4O_{10} and polyethylene glycol (PEG) (MW, ~ 1500) were purchased from Sigma-Aldrich. Firstly, solid PEG transformed into liquid by heating at 80°C in a vacuum oven. White powdered P_4O_{10} (2.5 g) was added into the above liquid PEG (7.5 g). After 40 min at 80°C in the vacuum oven, its color changed to black because the super absorbent P_4O_{10} extracted the water from PEG and polymerized to a long chain molecule of polyphosphoric acid, meanwhile the PEG was carbonized by losing H_2O . Subsequently, the intermediate products were transferred into an alundum boat (Fisher Scientific) and calcined at 900°C with a ramping rate of $15^\circ\text{C}/\text{min}$ and an argon flow rate of 5 sccm (Standard Cubic Centimeter per Minute) under sunlight. When some red substance appeared onto the inner wall of the quartz tube (about 0.5 h at

900°C), the boat was moved to the 250°C zone in the quartz tube and remained for 1 h under sunlight (Supplementary information, Fig. S1). The low temperature (250°C) was carried out to condense the produced red P, according to its melting point of 590°C . Sunlight catalyzes the production of red P instead of the toxic and flammable white P. The above mentioned procedure was repeated for 10 times. Finally, the P/C composite was obtained after washing with a 5% NaOH aqueous solution to remove the residual P_4O_{10} . For comparison, the carbon framework alone was obtained by oxidizing red P via heating at 350°C for 2 h in air, and then washing by a 5% NaOH aqueous solution to remove the phosphorus oxides. Pure red P was prepared in the same conditions by changing the Ar flow rate to 50 sccm, and collected from the inner wall of the quartz tube.

2.2. Electrochemical characterization

The battery performance was evaluated by galvanostatic cycling of coin (CR 2032) cells with the P/C composite as the working electrode and sodium foil as the counter/reference electrode. The working electrodes were made using a typical slurry method with P/C powders, carbon black and polyvinylidene fluoride (PVDF) binder with a mass ratio of 85:5:10 in N-methyl-pyrrolidone (NMP) solvent; the mass loading of active material (P/C composite) was $\sim 2.5\text{ mg cm}^{-2}$. The electrolyte consisted of 1.0 mol L^{-1} $NaPF_6$ in an ethylene carbonate (EC)-diethyl carbonate (DEC) solution with addition of 10% fluoroethylene carbonate (FEC) in order to form a stable SEI film. [27] The electrochemical data were collected using an Arbin MSTAT battery test system within the potential range $0.01\text{--}1.5\text{ V}$ (vs. Na/Na^+) at various current densities. The specific capacity was calculated based on the total weight of phosphorus and carbon.

3. Results and discussion

The process for the fabrication of the P/C composite, featuring ultrafine red P particles (~ 10 nm) embedded in 3D carbon matrix, is schematically depicted in Fig. 1. Firstly, white P_4O_{10} particles were coated with a polymer shell of PEG in a vacuum oven at 80°C (Fig. 1a). Tens of minutes later (Fig. 1b), the mixture turned black due to dehydration and subsequent carbonization of the PEG.

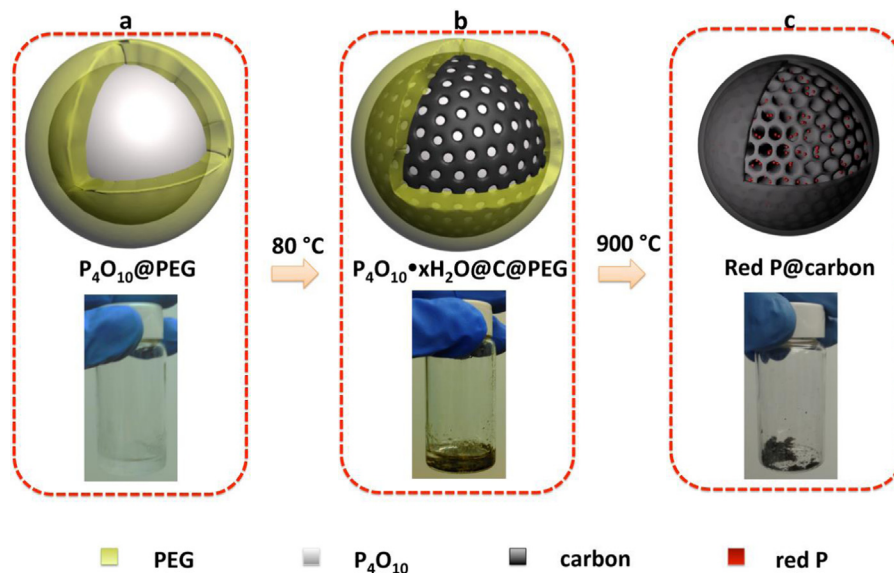


Fig. 1. Schematic and digital photographs of the synthesis procedure for the ultrafine red phosphorus particles embedded in a 3D carbon framework (P/C composite). (a) P_4O_{10} coated with PEG. (b) $P_4O_{10} \cdot xH_2O$ coated with carbon and PEG. (c) the P/C composite.

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