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Electrochemical Performance of Iron Diphosphide/Carbon Tube Nanohybrids in Lithium-ion Batteries

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ABSTRACT

Phosphorous-rich phase iron diphosphide/carbon tube (FeP_2/C) nanohybrids, which are synthesized via a pyrolysis process and composed of heterostructures of orthorhombic FeP_2 with conical carbon tubes, have been identified as a new anode in lithium-ion batteries. After an annealing treatment to eliminate the excessive hydrogen elements in the carbon tubes, the FeP_2/C nanohybrids display good reversible capacity, long cycle life, and excellent rate capability. Specifically, the annealed hybrids exhibit a discharge capacity of 602 mA h g^{-1} on the second cycle and a discharge capacity of 435 mA h g^{-1} after 100 cycles at 0.1C (0.137 A g^{-1}). Meanwhile, these annealed hybrids exhibit excellent rate capability, such as a reversible capability of 510 mA h g^{-1}, 440 mA h g^{-1}, 380 mA h g^{-1}, 330 mA h g^{-1} and 240 mA h g^{-1} at 0.25C, 0.5C, 1C, 2.5C and 5C, respectively.

1. Introduction

Nowadays, transition-metal phosphides are emerging as an appealing class of materials in the field of magnetism [1a–d], electronics [2], catalysis [3a–d], energy storage [4a,b] and even biology and medicine applications [5a,b]. Especially, the phosphorus-rich TMPs [6,7] have received numerous interests as viable anode materials in lithium-ion batteries (LIBs) due to their much higher theoretical capacities as compared to graphite. FeP_2, a representative member of the phosphorus-rich TMPs is expected to be a promising kind of anode materials because of its high theoretical capacity (1365 mA h g^{-1}) and natural abundance, which are well satisfied for the high energy density and low cost demands of the LIBs system. In addition to the aspects of energy density and material cost, other performance parameters, such as cycle life and rate capability are also vital links for the LIBs system. Unfortunately, from the existing electrochemical results of the bulk FeP_2 [8,9], it is easy to find that there are two distinct drawbacks of rapid capacity fading and short cycle-life existing in this kind of anode materials for the FeP_2-based LIBs system. And also, detailed investigations reveal that these drawbacks are primarily caused by the irreversibility of the conversion reaction, the large volume changes during the charge-discharge process and the much lower conductivity of FeP_2 phase compared with the carbon anodes. Recently, amorphous FeP_2 nanopowders, which are synthesized by a low-temperature route exhibit a discharge capacities of 1258 mA h g^{-1} on the first cycle and a discharge capacity of 906 mA h g^{-1} after 10 cycles [10]. This result indicates that the amorphous structure of FeP_2 may be an optional strategy to buffer volume changes and prevent degradation processes during the cycling. However, amorphous FeP_2 nanopowders are unstable thermodynamically in general and the process of synthesis and fabrication have to handle without any air exposure, otherwise, a drastic capacity reduction of the amorphous FeP_2 would happen. Besides the above-mentioned strategy, many pioneering works [11a–c,12a,b] have also shown that the nanostructured crystalline material and/or with a conductive layer (usually carbon) can substantially buffer the volume change and improve the conductivity of the active material during the cycling, which are efficient strategies to maintain good capacity retention and prolong cycle life. So, to prepare crystalline FeP_2 with well-defined nanostructures and/or with carbon coatings is of great significance to further improve their lithium storage performance.

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Very recently, we have developed a facile one-pot synthetic route to phosphorous-rich phase FeP_2/C nanohybrids that are prepared from reaction of ferrocene ($Fe(C_5H_5)_2$) with red phosphorus at 500 °C, which demonstrates high performance for catalysis of hydrogen evolution reaction [13a]. Interesting, these hybrids are composed of heterostructures of orthorhombic FeP_2 with conical carbon tubes. As noted, the nanostructured FeP_2/C hybrids would be of advantageous for capacity retention and rate capability in the LIBs system since that both the nanostructured form of FeP_2 and the hybridized carbon can relieve the volume change and improve the transport properties of the FeP_2-based anode materials [14a–c]. As expected, after an annealing treatment to eliminate the excessive hydrogen elements, which may despair the carbon tubes during the discharge/charge process [15a–c], the FeP_2/C nanohybrids overcome the rapid capacity fading and display a remarkable rate capability, making them a promising anode material for lithium-ion batteries.

2. Experimental section

2.1. Materials

Ferrocene ($Fe(C_5H_5)_2 \geq 95\%$) is purchased from Alfa Aesar. Red phosphorus (powder, 99% purity) and solvent of ethanol are all obtained from Shanghai Chemical Reagents Company, China. All reagents are used as received without further purification.

2.2. Synthesis of FeP_2/C nanohybrids

Synthetic procedures to the FeP_2/C nanohybrids are adopted from our previous work [13a,b], and the details are described as below. In a typical synthesis, a mixture of 0.112 g (~0.6 mmol) of Fe $(C_5H_5)_2$ and 0.038 g (~1.2 mmol) of red phosphorus is tableted and put into a quartz tube (φ8 mm × 150 mm), which is then evacuated and sealed. The tube is loaded into a resistance furnace

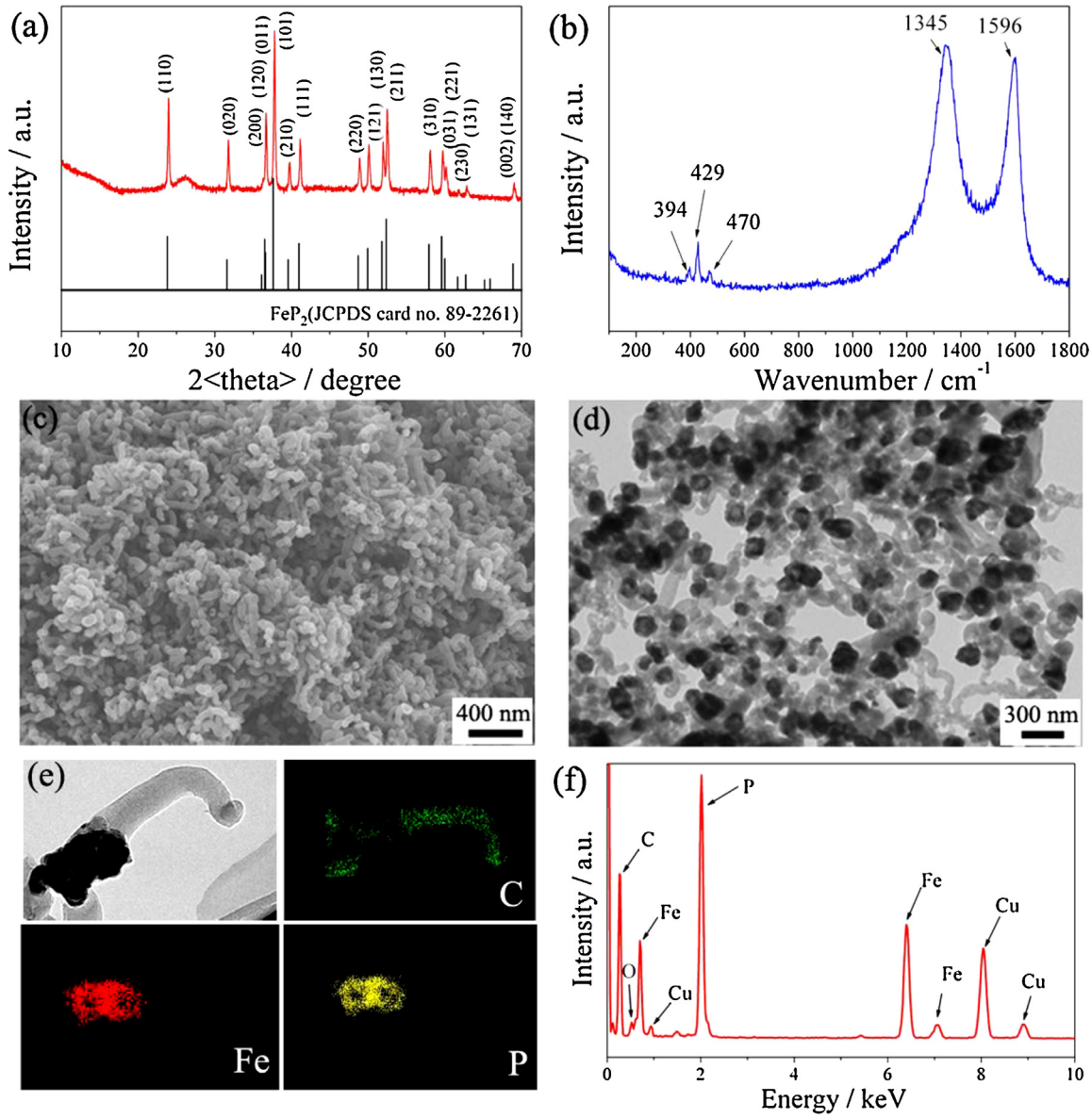

Fig. 1. (a) Powder XRD pattern for the annealed FeP_2/C nanohybrids (red, top) and the standard pattern of FeP_2 (JCPDS card no. 89-2261) (black, bottom), (b) Raman spectroscopy, (c) SEM, (d) TEM images for the annealed FeP_2/C nanohybrids, (e) the corresponding EDX mapping of the hybrid. Different colours are applied to distinguish the position of the elements, C (green), Fe (red) and P (yellow), respectively, and (f) the EDX spectra for the annealed FeP_2/C nanohybrids, and the signal of Cu arises from the TEM grid.