



Developing porous carbon with dihydrogen phosphate groups as sulfur host for high performance lithium sulfur batteries



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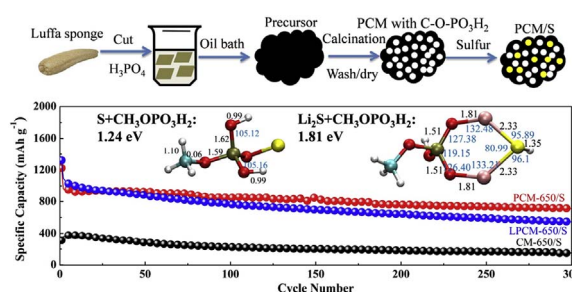
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HIGHLIGHTS

- Porous carbon (PCM-650) is prepared from luffa sponge using H_3PO_4 as activator.
- PCM-650 as sulfur host in Li-S battery exhibits excellent cycling performance.
- The cycling performance is relative to dihydrogen phosphate groups (DPG) of PCM-650.
- The effect of DPG is investigated by density functional theory calculation and XPS.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon matrix (CM) derived from biomass is low cost and easily mass produced, showing great potential as sulfur host for lithium sulfur batteries. In this paper we report on a dihydrogen phosphate modified CM (PCM-650) prepared from luffa sponge (*luffa acutangula*) by phosphoric acid treatment. The phosphoric acid not only increases the surface area of the PCM-650, but also introduces dihydrogen phosphate onto PCM-650 (2.28 at% P). Sulfur impregnated (63.6 wt%) PCM-650/S, in comparison with samples with less dihydrogen phosphate LPCM-650/S, shows a significant performance improvement. XPS analysis is conducted for sulfur at different stages, including sulfur (undischarged), polysulfides (discharge to 2.1 V) and short chain sulfides (discharge to 1.7 V). The results consistently show chemical shifts for S_{2p} in PCM-650, suggesting an enhanced adsorption effect. Furthermore, density functional theory (DFT) calculations is used to clarify the molecular binding: carbon/sulfur (0.86 eV), carbon/ Li_2S (0.3 eV), $CH_3-O-PO_3H_2$ /sulfur (1.24 eV), and $CH_3-O-PO_3H_2/Li_2S$ (1.81 eV). It shows that dihydrogen phosphate group can significantly enhance the binding with sulfur and sulfide, consistent with XPS results. Consequently a CM functionalised with dihydrogen phosphate shows great potential as the sulfur host in a Li-S battery.

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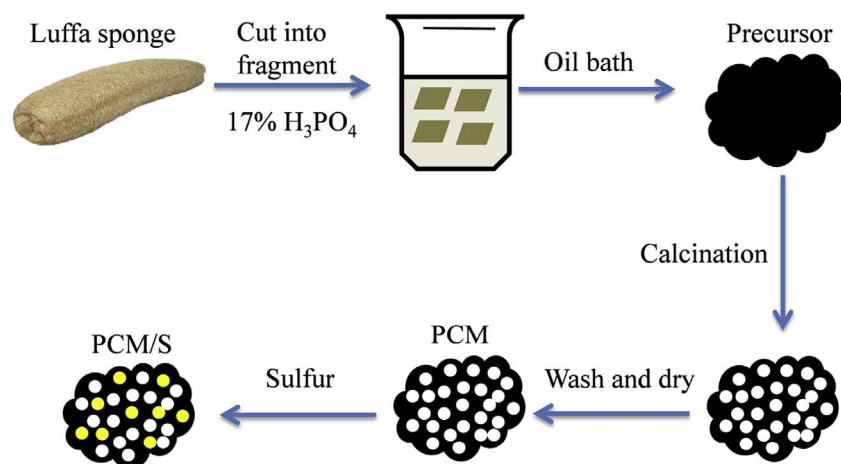


Fig. 1. Schematic drawing of PCM/S preparation.

1. Introduction

Batteries have been widely used in various fields such as electric vehicles, portable electronic devices, microchips, and energy storage system [1–3]. Among various batteries technology, the lithium ion battery occupies the highest market share, however, the limited energy density requires novel electrode materials or alternative strategies [4,5] and the lithium sulfur (Li-S) battery is one of the alternatives [6–10]. The theoretical energy density can reach 2600 Wh kg^{-1} , which is $\sim 3\text{--}5$ times that of the traditional lithium ion battery [11,12]. In addition, sulfur has many advantages such as, high specific capacity (1672 mAh g^{-1}), low cost, and it is also eco-friendly [13]. However, its development and application is restricted by several main issues [14,15]. Firstly, sulfur is an insulating cathode material ($\sim 10^{-30} \text{ S cm}^{-1}$) and the final products after discharge (Li_2S_2 and Li_2S) are also poorly conductive [16]. Secondly, an inevitable volume change occurring during charge and discharge can damage the structure of cathode and affect the cycling performance [17]. Thirdly, the polysulfide produced during charge and discharge is easily dissolved in electrolyte [18–20], and result in the “shuttle effect” [21,22] which will reduce the mass of active material, decrease the coulombic efficiency, and deteriorate cycling performance [23–25]. A high porosity carbon matrix (CM), as the sulfur host, can enhance conductivity of sulfur and accommodate volume change, therefore, it can relieve the initial two issues mentioned above [26–28]. Carbon matrixes derived from biomass materials are low cost and allow production on a large scale which are beneficial to promoting the application of Li-S batteries [29–31].

However, the CM with homogeneous nonpolar surface served as host for sulfur cannot afford a sufficient binding and restraining effect to hold lithium polysulfides within the cathode. DFT calculation has approved that the chemical modification using N or O element can significantly enhance the interaction between the carbon surface and the polysulfide by dipole-dipole electrostatic interaction, and then restrain shuttle of polysulfides effectively [32]. The calculations have been attested by publications, which show the N/O-doped carbon can trap soluble polysulfides and restrain the shuttle effect [33–42]. Meanwhile the DFT calculations also showed that monodopant (such as, boron, phosphorus and sulfur) into carbon matrix is unsatisfactory and cannot offer improved performance [32]. However, by co-doping with O or N, the dopants (boron, phosphorus or sulfur) can synergistically strengthen the dipole moment and enhance the interaction between the carbon surface and the polysulfide, such as (B, O) co-dopant [43], (N, S) co-dopant [44,45], and (N, P) co-dopant [46,47]. It's worth noting that, among these co-dopant, (O, P) has been barely investigated, especially the phosphate groups.

In this paper a porous carbon matrix is prepared using luffa sponge (*luffa acutangula*) as the carbon source due to its abundance and high

surface area [48], followed by modification (PCM-650) with phosphate groups through phosphoric acid activation [49–51]. The electrochemical performances had been compared between PCM-650 (2.28 at % P), low phosphate groups CM (LPCM-650, 1.08 at% P) and none phosphoric acid treated CM (CM-650). In order to explore the effect of phosphate groups, XPS and DFT calculations was used to study the binding energies with sulfur/sulfide. The results show an enhanced adsorption between sulfur/sulfides and phosphate group, therefore, PCM-650/S exhibits an improved electrochemical performance.

2. Experimental section

2.1. Materials preparation

5 g cleaned luffa sponge (*luffa acutangula*) was dipped in 100 ml phosphoric acid (H_3PO_4) solution (17 vol%), then heated in an oil bath at 70°C for 10 h and 120°C for another 10 h. The obtained black bulk was placed in graphite boats and heated at 550°C , 600°C , and 650°C respectively for 2 h in tube furnace filled under N_2 atmosphere. Then the bulk was dipped into 1 mol L^{-1} HCl solution and boiled at 90°C for 3 h, followed by vacuum filtration and washing with hot distilled water and ethanol. Eventually the phosphorous modified porous carbon (PCM) was obtained after dried at 80°C for 12 h and grounded into powder. The PCM, carbonized at 550°C , 600°C and 650°C , are referred to as PCM-550, PCM-600, and PCM-650, respectively. Also, to allow comparison, a sample (CM-650) was prepared, using the same conditions as PCM-650, but without treating with a solution of H_3PO_4 .

In addition, to verify the effect of the phosphorous modification, PCM-650 was calcined at 900°C for 2 h with nitrogen atmosphere and the resulting sample is referred to as LPCM-650 (low concentration phosphate groups carbon matrix).

The PCM/S composite was prepared by melt-diffusion method and the schematic drawing of the entire process is shown in Fig. 1. PCM and sulfur powder were mixed uniformly with a mass ratio of 1:2 and then heated at 155°C for 10 h in the tube furnace under flowing N_2 gas. Finally the PCM was completely impregnated with sulfur and the PCM/S composite was obtained.

2.2. Material characterization

The morphology and structure of samples were characterized by scanning electron microscope (SEM, HITACHI S-4700), Raman spectroscopy (Renishaw RM-1000), X-ray diffraction (XRD, Rigaku D/Max 2500/PC), and transmission electron microscope (TEM, JEM-2100HR). The specific surface area, pore volume and pore size distribution of PCM were obtained by using Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model with a surface area and pore

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