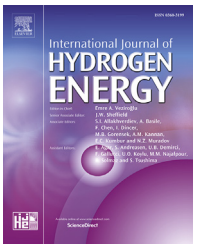
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–9

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Polyaniline@spherical ordered mesoporous carbon/sulfur nanocomposites for high-performance lithium-sulfur batteries

Ze-Wen Ding, Dong-Lin Zhao, Ran-Ran Yao, Cheng Li, Xing-Wang Cheng, Tao Hu*

State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers (Beijing University of Chemical Technology), Ministry of Education, Beijing Engineering Research Center of Environmental Material for Water Purification, Beijing University of Chemical Technology, Beijing, 100029, China

ARTICLE INFO

Article history:
Received 11 March 2018
Received in revised form
17 April 2018
Accepted 19 April 2018
Available online xxx

Keywords:
Polyaniline
Spherical ordered mesoporous carbon
Electrochemical performance
Lithium-sulfur battery

ABSTRACT

Lithium-sulfur batteries have attracted a lot of attention in the recent years. However, the electrochemical performance of lithium-sulfur batteries is greatly affected owing to several issues. In this paper, we designed a polyaniline@spherical ordered mesoporous carbon/sulfur nanocomposite (PANI@S-OMC/S), and S-OMC/S was wrapped by PANI via in-situ polymerization. The inherently conducting nature of PANI increased conductivity of PANI@S-OMC/S electrode to improve the free transfer of electrons, and PANI shell also provided a barrier between the lithium polysulfides and electrolyte to further prevent the occurrence of the "shuttle effect". Moreover, mesoporous pores are wonderful hosts to contain sulfur to trap the long-chain lithium polysulfides and prevent them from dissolving in electrolyte. A high initial discharge capacity of 1626 mAh/g was achieved for the PANI@S-OMC/S electrode in first cycle at 0.1 C, and the composite maintains 1338 mAh/g after 100 cycles while the coulombic efficiency still remains ~98%.

Introduction

The emergence of the energy crisis prompted the advent of Lithium ion battery. Lithium ion battery is the most widely used electronic products in the market at present, and it is also the main research direction of high energy density storage applications [1]. A lot of hard work has been made to improve the energy density and electrochemical performances of lithium ion batteries in recent 20 years, however, the theoretical specific capacity is limited by the cathode material [2], which is difficult to meet the needs of the development. Sulfur is one of the most plentiful elements on earth at present, lithium sulfur batteries have become one of the most widely studied lithium ion battery systems due to the high theoretical energy density (~2500 W h/kg) and the high theoretical specific capacity (~1673 mA h/g), as well as their safety and low cost [3–7]. However, some serious problems have hindered the application and commercialization of lithium-sulfur batteries, these problems include: (1) Sulfur

* *Corresponding author.*
E-mail address: dlzhao@mail.buct.edu.cn (D.-L. Zhao).

https://doi.org/10.1016/j.ijhydene.2018.04.134
0360-3199/

and its discharge products (Li_2S/Li_2S_2) are typical ionic and electronic insulators [5,7–9]. (2) The dissolution of lithium polysulfides (LPS) into electrolyte brings on fast decline of specific capacity and low coulombic efficiency [5,7–9]. (3) In the process of discharge/charge, the sulfur-based cathode expands and contracts in succession, which causes the damage and collapse of structure [5,7–10].

A lot of hard work [11–21] has been made to solve above issues, carbon host materials such as carbon nanotubes [11], hollow carbon tubes [12,13], graphene [14–17], porous carbon spheres [18] and hollow carbon spheres [19], as well as polymeric host materials [20] such as polypyrrole (PPY) [21,22], polydopamine [23], polyaniline (PANI) [24,25] have been used and applied to ameliorate the conductivity and discharge capacity of lithium-sulfur batteries, heteroatom modification are also reported to improve lithium–sulfur batteries [2]. Ji and coworkers make the sulfur to load on the graphene oxide via a simple chemical reaction, and remove excess of elemental sulfur at 155 °C under argon atmosphere [14]. Zhou and coworkers report the synthesis of yolk–shell PPY/S nanocomposites via a heating vulcanization core–shell structure [21]. Unfortunately, recent report presents that carbon host materials have low binding energy with polar Li_xS ($0 < x \leq 2$) [26]. Polymeric host materials cannot meet the need of the special structure to constrain sulfur generally. In summary, an additional layer of conductive polymer coating on the carbon host cathode materials for sulfur cathodes was necessary to address the key problems of lithium-sulfur batteries.

As far as we know the spherical ordered mesoporous carbon nanoparticles wrapped by polyaniline as sulfur-based materials for lithium-sulfur batteries have not been reported yet. As one of the promising conductive polymers, the conductivity of PANI is excellent. The conducting nature of PANI can facilitate electronic conduction, moreover, the flexible nature of PANI can reduced volumetric effect effectively [3]. Previous study showed the interaction between Li_2S and the functional groups in macromolecular binders greatly affected the cycling stability of Li_2S cathode. As to PANI, we can see that both oxygen and sulfur atom strongly bind with the lithium atom in Li_2S to form a chelated coordination structure. This very stable configuration gives a strong binding energy of 0.67 eV [27]. Therefore, we designed a polyaniline@spherical ordered mesoporous carbon/sulfur nanocomposite (PANI@S-OMC/S). S-OMC/S was wrapped by PANI via in-situ polymerization, the inherently conducting nature of polyaniline can increase conductivity of cells to improve the free transfer of electrons, and the PANI shell also can provide a barrier between the lithium polysulfides and electrolyte to further prevent the occurrence of the "shuttle effect", moreover, mesoporous pores are wonderful hosts to contain sulfur to trap the long-chain lithium polysulfides and prevent them from dissolving in electrolyte. The S-OMC/S and PANI@S-OMC/S that we designed show the excellent electrochemical performance, at 0.1 C rate, a high initial discharge capacity is achieved for the PANI@S-OMC/S electrode in first cycle, which is approaching theoretical capacity. The PANI@S-OMC/S composite maintains stable after 100 cycles while the coulombic efficiency still remains ~90%.

Experimental

Synthesis of spherical ordered mesoporous carbon nanoparticles

All the chemicals were bought from Sigma-Aldrich in ACS reagent. For the Si/P123/N-butyl alcohol slurry 4 g P123 (polyethylene oxide–polypropylene oxide–polyethylene oxide) was add to 120 ml 0.9 M $H_2S_2O_4$ (Sulfuric acid) aqueous solution under magnetic stirring at 35 °C. Then 2.5 ml N-butyl alcohol ($CH_3(CH_2)_3OH$) were added under magnetic stirring for 1 h, followed by the addition of 8.3 ml TEOS (tetraethyl orthosilicate) for 12 min under magnetic stirring. The static reaction proceeded at 35 °C for 24 h to form the suspension, the suspension was transferred into a 50 ml Teflon-lined stainless steel autoclave which was heated up to 100 °C for 24 h. After the reactions were completed, the white product was filtered and dried in a vacuum oven at 60 °C for 24 h.

For the spherical SiO_2/Carbon Nanoparticles the material was carbonized at 850 °C in nitrogen, the heating sequence was 2 °C/min to 850 °C.

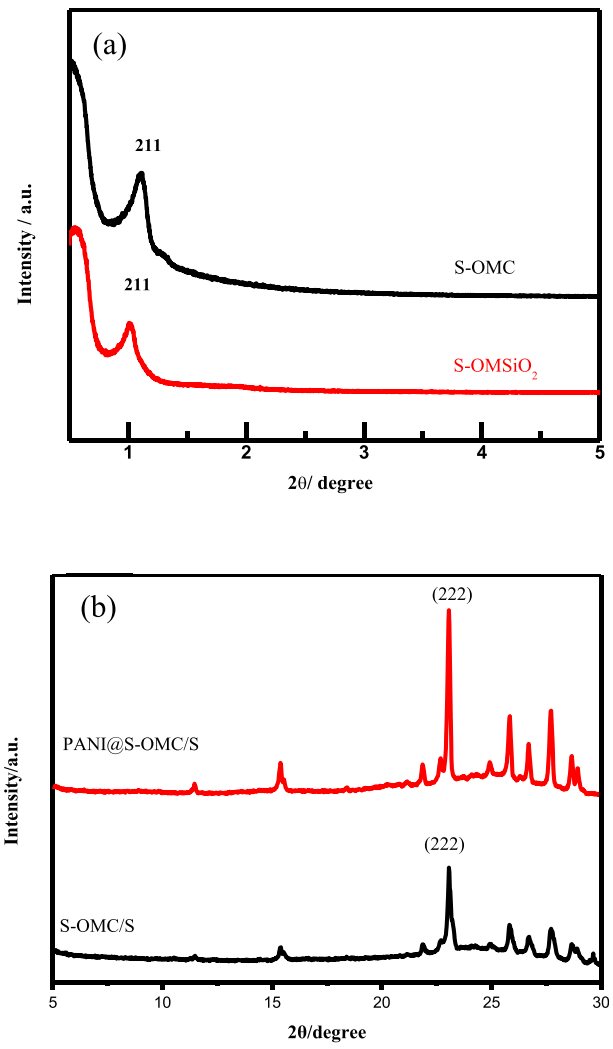


Fig. 1 – (a) XRD patterns of S-OMC and S-OMSiO$_2$ (b) XRD patterns of S-OMC/S and PANI@S-OMC/S.

Please cite this article in press as: Ding Z-W, et al., Polyaniline@spherical ordered mesoporous carbon/sulfur nanocomposites for high-performance lithium-sulfur batteries, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.04.134