Electrochimica Acta 109 (2013) 145–152

Contents lists available at ScienceDirect

Electrochimica Acta

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

# A ternary sulfur/polyaniline/carbon composite as cathode material for lithium sulfur batteries

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ARTICLE INFO

*Article history:*
Received 17 April 2013
Received in revised form 28 June 2013
Accepted 12 July 2013
Available online 20 July 2013

*Keywords:*
Polyaniline
Ternary composites
Cathode material
Lithium sulfur batteries

ABSTRACT

A ternary sulfur/polyaniline–carbon (SPC) black composite was prepared by combining elemental sulfur and polyaniline–carbon black (PANi-C) composite by a continuous two-step thermal treatment at 155 °C and 280 °C. SPC composites were characterized by field emission scanning electron microscopy, transmission electron microscopy, X-ray diffractometer, Raman spectroscopy, Fourier transformation infrared spectroscopy and X-ray photoelectron spectroscopy. PANi-C is a highly conductive polymer–carbon composite with PANi impregnated in porous carbon. PANi plays a bridge role between sulfur and carbon in SPC composites, resulting in the minimization of active material loss and the improvement of electrochemical performance in lithium sulfur batteries. The cell with SPC composite as cathode showed enhanced cyclablity and good rate capability, retaining a discharge capacity of 732 mAh $g^{-1}$ at 0.2 C after 100 cycles.



## 1. Introduction

There has been a challenge to develop and design lithium batteries with high specific energy for the requirement of an increasingly diverse range of applications from microchips to cars and electric energy storage systems. Lithium sulfur (Li—S) batteries have received great attention due to their high theoretical capacity, easy availability, low cost and non-toxicity [1]. The combination of lithium metal with theoretical specific capacity of 3830 mAh $g^{-1}$ as anode and elemental sulfur ($S_8$) with theoretical specific capacity of 1675 mAh $g^{-1}$ as cathode in a battery can generate theoretical specific energy as high as 2600 Wh $kg^{-1}$, more than 5 times higher than the theoretical energy of commercial lithium ion batteries [2].

Although the studies on Li—S batteries could be traced back to the 1960s [3], many challenges are encountered for the practical realization of Li—S batteries. The insulating nature of both sulfur and its reduction product, lithium sulfide, leads to low active material utilization [4]. Moreover, the soluble lithium polysulfides ($Li_2S_x$, $4 \le x \le 8$) generated during the discharge process can easily escape from the electrode to the liquid electrolyte (termed as "shuttle" phenomenon), resulting in a loss of active material and an increase of resistance in cells [5]. Many efforts have been made to overcome these drawbacks. It has been reported that lithium nitrate as an additive to the liquid electrolyte can effectively relieve the shuttle effect by passivating lithium anode [6]. Fabrication of sulfur/carbon composites is another alternative way in which conductive carbon matrices with some featured structures have been constructed to disperse sulfur and hold the soluble polysulfides. A variety of carbon materials such as porous carbons [7–10], carbon nanotubes [11,12], graphene nanosheets [13,14], hollow carbons [15] and carbon fibers [16,17] have been widely investigated and their application in composites greatly improved the electrochemical performance by increasing utilization and retention capacity of sulfur as an active material.

Conducting polymers such as polypyrole (PPy) [18], polythiophene (PTh) [19], poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) [20] and polyaniline (PANi) [21–23] have been successfully used in sulfur composites either as a coating layer or a conductive matrix to improve the cycle performance and rate capability of Li—S batteries. Especially, PANi is widely used owing to its relatively facile processability, electrical conductivity and environmental stability [24]. PANi nanotubes have been reported to provide strong chemical confinement to sulfur and resident polysulfides by forming C—S bonds at 280 °C which alleviate the volume expansion during electrochemical reactions from sulfur to lithium sulfide [21]. Due to the relatively lower conductivity of PANi than carbon, the decrease in overall electric conductivity of the composite can be a drawback for increasing the capacity at higher current density. However, a PANi coated sulfur/carbon

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http://dx.doi.org/10.1016/j.electacta.2013.07.067

composite with a core–shell structure was proved to deliver a high-rate charge/discharge capability resulting from the high electrical conductivity from both the conductive carbon black in the core and PANi in the shell [23].

Incorporating carbon with PANi makes it a promising material for both capacitors and sensors with superior electrical properties [25–27]. PANi/MWNT composite has attracted intense interests since MWNT can be well dispersed in PANi matrix with enhanced processability and PANi can also strongly interact with MWNT through charge-transfer to obtain enhanced conductivity [28]. Mesoporous carbons with high surface area and mechanical strength have been exploited to prepare PANi composites in which PANi is coated at both external and internal surface of porous carbon. Excellent performance with 25 wt.% PANi in ordered mesoporous carbon was reported for electroanalytical sensors [29].

Here, we report the use of commercially available porous PANi–carbon black (PANi-C) composite as a conducting framework for housing sulfur. PANi-C is a conductive polymer–carbon composite with 20 wt.% PANi on carbon black. PANi is informed to be doped with organic sulfonic acid and located on the outside surface as well as the inside pores of carbon black. It has a high conductivity of 30 S $cm^{-1}$ and a high surface area to provide a good electric conductor for sulfur cathodes. It is believed that both porous carbon and flexible PANi aid in high utilization of active material and improved electrochemical properties of Li—S cells with sulfur/PANi-C (SPC) composite as cathode material.

## 2. Experimental

To prepare SPC composites, elemental sulfur (99.98%, Aldrich) and PANi-C (20 wt.% PANi on carbon black, Aldrich) were mixed in a PTFE jar by ball milling at a certain weight ratio. The mixture was heated at 155 °C for 12 h and then at 280 °C for 12 h in $N_2$ atmosphere.

The surface morphology of the composites was observed with field emission scanning electron microscope (FE-SEM, Philips XL30S FEG) and transmission electron microscope (TEM, JEM2010 JEOL). Brunauer–Emmett–Teller analysis (BET, ASAP 2010) was

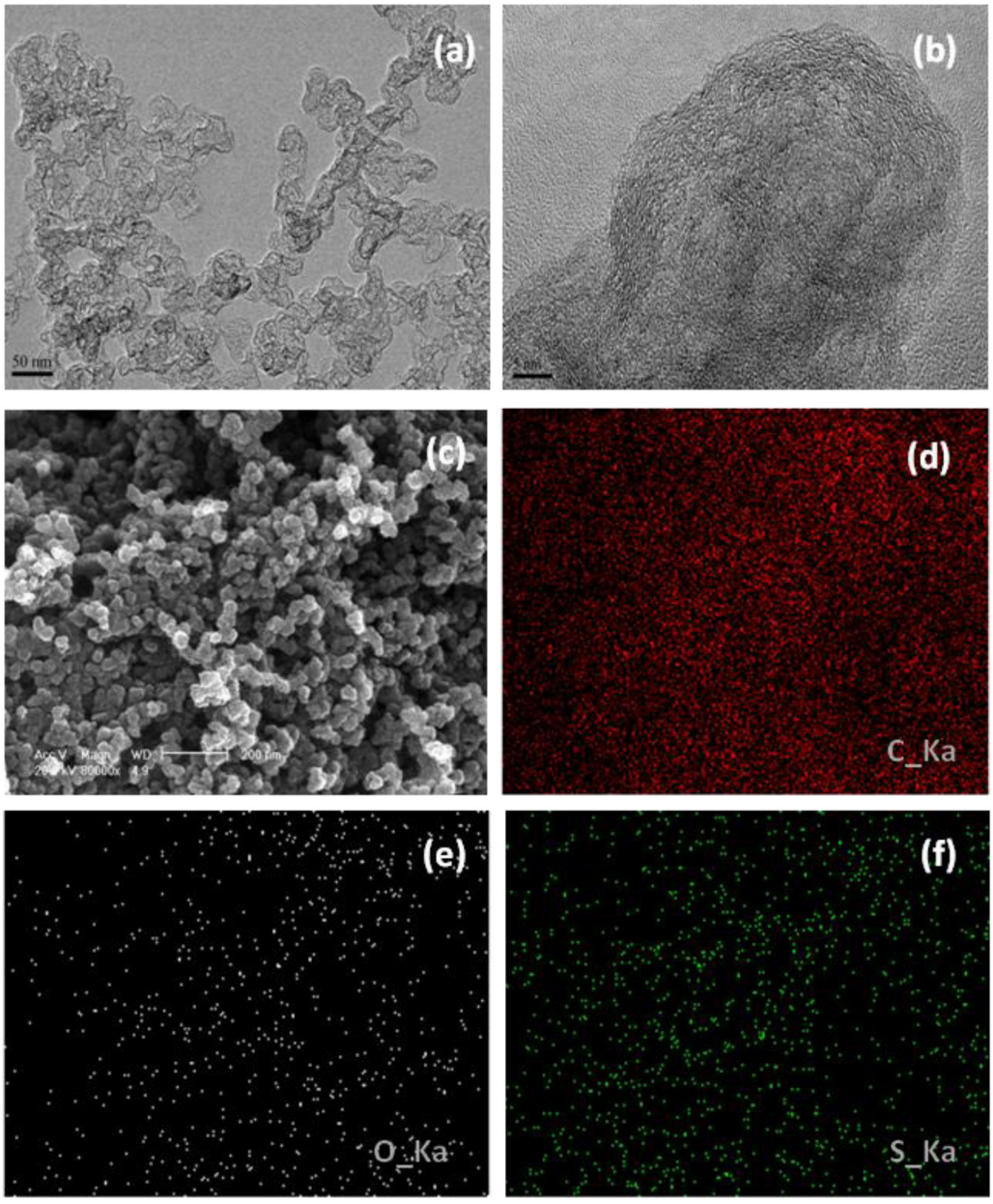


**Fig. 1.** Morphology of PANi-C observed by (a and b) TEM and (c) FE-SEM, and its EDS elemental mapping of (d) carbon, (e) oxygen and (f) sulfur.