



## Key parameters in design of lithium sulfur batteries



Ning Ding<sup>a</sup>, Sheau Wei Chien<sup>a</sup>, T.S. Andy Hor<sup>a,b</sup>, Zhaolin Liu<sup>a,\*</sup>, Yun Zong<sup>a,\*</sup>

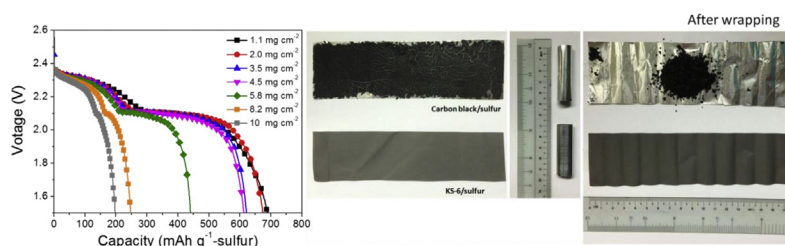
<sup>a</sup> Institute of Materials Research and Engineering (IMRE), A\*STAR (Agency for Science, Technology and Research), 3 Research Link, Singapore 117602, Republic of Singapore

<sup>b</sup> Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Republic of Singapore

### HIGHLIGHTS

- Studied the effect of the carbon to sulfur ratio on the performance of Li–S batteries.
- Investigated the influence of sulfur loading density and electrolyte volume on cell capacity.
- Provided a guideline for the design of high performance Li–S batteries.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 21 May 2014

Received in revised form

25 June 2014

Accepted 1 July 2014

Available online 9 July 2014

#### Keywords:

Lithium sulfur battery

Carbon to sulfur ratio

Sulfur loading density

Electrolyte volume

Deformability

### ABSTRACT

In this paper, we discuss some key parameters in design of lithium sulfur batteries with high energy density, in particular carbon/sulfur ratio, sulfur loading density, electrolyte volume and electrode deformability, which directly impact the battery performance in terms of capacity, cycleability, and processibilities, etc. We find that a carbon to sulfur ratio of 1:2 (w/w) in the electrode is good for high specific capacity, giving a capacity of  $538 \text{ mA h g}^{-1}$  which is 3 times as high as that of  $\text{LiCoO}_2$  cathode. The issue of fragileness for electrode at high sulfur loading density is mitigated by replacing carbon black with fine graphite powders. With these optimizations the carbon–sulfur electrode gives an energy density of  $5.88 \text{ mW h cm}^{-2}$  which corresponds to 60% of that of the commercial  $\text{LiCoO}_2$  electrode.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Lithium-ion (Li-ion) batteries have dominated the power supply market of portable electronic devices since the first launch of commercial lithium cobalt oxide/carbon ( $\text{LiCoO}_2/\text{C}$ ) cells by Sony in 1991. Though being widely used the Li-ion batteries are seeing their bottlenecks in energy density limited by the lithium capability of lithium transition metal oxide (Li–M–O, M = Ni, Co and Mn) cathodes which typically deliver a theoretical specific capacity in the

range of  $120\text{--}320 \text{ mA h g}^{-1}$  [1,2]. To meet the ever-growing demands on rechargeable batteries with higher energy density, non-lithium intercalated transition metal oxides, such as  $\text{Me}_x\text{O}_y$  (Me = V [3–5] or Cr [6]) and group 16 (VIA) elements (primarily oxygen [7], sulfur [8] and selenium [9]), have recently been exploited as the cathode materials for next-generation lithium batteries. For these non-lithium intercalated cathodes, lithium is used as the counter anode. In this case extra care in safety is required, as the growth of dendrites may cause short-circuit and explosion if the electrode is not properly engineered. Lithium–sulfur (Li–S) system is considered as the safest among batteries using lithium metal as anode, as its discharged products, lithium polysulfides, are soluble in the electrolyte that significantly suppress the formation of lithium dendrites [10]. Li–S battery is also a choice for its high energy

\* Corresponding authors.

E-mail addresses: [zl-liu@imre.a-star.edu.sg](mailto:zl-liu@imre.a-star.edu.sg) (Z. Liu), [y-zong@imre.a-star.edu.sg](mailto:y-zong@imre.a-star.edu.sg) (Y. Zong).

density. Theoretically, sulfur can deliver a specific capacity of 1672 mA h per gram sulfur ( $\text{mA h g}^{-1}$ -sulfur) that is nearly 5 times as high as that of Li-ion batteries [11]. Furthermore, Li–S battery is a cost-effective choice, as sulfur is obtained from the byproducts of oil refining with the annual world production of 69 million tons (Mt) in 2011 [12] which is sufficient for 4 billions of 60 kW automobiles.

So far, major efforts in the Li–S battery research have been the development of sulfur composites with various microstructures for the cathode, and some interesting findings were reported [13–23]. For sulfur cathode, one has to deal with its poor intrinsic electrical conductivity ( $1 \times 10^{-15} \text{ S m}^{-1}$ ) by incorporating large portion of carbon black, which lowers the sulfur content and reduces the gravimetric and volumetric energy density at cell level [24]. High sulfur content (up to 70 wt%) can be achieved by incorporating sulfur into highly ordered mesoporous carbon, followed by coating with polyethylene glycol [25], or using a lower load of graphene or carbon nanotubes as substitute of carbon black [26–30]. More recently, the concept of forming a yolk-shell structure with internal void space to tolerate the volume expansion of sulfur during discharge was proposed by Cui et al. [13,23,31] and the composites exhibited distinctly improved cycling performance (>1000 cycles). Though these new cathode materials shed a light on Li–S battery research, the actual progress was far insufficient for practical application. For example, in these studies the sulfur loading density was less than  $1 \text{ mg cm}^{-2}$  [32–38]. In this case the theoretical overall cathode capacity per unit area is about 60% of that of  $\text{LiCoO}_2$  cathode in a commercial Li-ion batteries and the energy density is merely about 35% due to the lower working voltage of Li–S system. To compete with lithium-ion batteries using  $\text{LiCoO}_2$  electrode, one would need a minimum sulfur loading density of  $3 \text{ mg cm}^{-2}$  in the cathode. Some high sulfur loading density cases have been reported [39–42]; however, a high sulfur loading density often associates with mechanical failure of the electrode film, e.g. cracking and/or peeling, leading to poor battery performance. It remains a challenge to develop high quality sulfur electrode for high performance Li–S batteries.

Apart from cathode materials, the selection of electrolyte is crucial for Li–S batteries [43]. The electrolyte is the media that transports lithium ions and dissolves polysulfides (PS) which significantly impacts the overall electrochemical performances of Li–S battery [44]. Electrolyte with low viscosity and high PS solubility generally favors the cell reaction; however, the dissolution of PS imposes negative impact on coulombic efficiency and capacity retention. Such negative impact can be suppressed by the introduction of  $\text{LiNO}_3$  additive into the electrolyte [45]. During the discharge process, sulfur is gradually reduced to soluble PS ( $\text{Li}_2\text{S}_8$ ,  $\text{Li}_2\text{S}_6$  and  $\text{Li}_2\text{S}_4$ ).  $\text{Li}_2\text{S}_4$  is further reduced to insoluble sulfides ( $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$ ) that precipitate on the carbon surface at the end of discharge. In the reversed charge process, insoluble PS is first oxidized into soluble PS which is further converted into sulfur and eventually precipitates on the carbon surface when charge is completed. The excess amount of PS in the electrolyte may cover the sulfur surface as a nonconductive coating and adversely impact the following discharge performance. Moreover, the amount of electrolyte also affects the cell performance. Larger volume of electrolyte generally leads to a higher initial discharge capacity [46]; however, it reduces the energy density of the cell. Therefore, it is critical to balance the volume of electrolyte and the amount of sulfur for high performance Li–S batteries.

In this work, we prepared a series of carbon/sulfur (C/S) composites with a different weight ratio (3:1, 2:1, 1:1, 1:2 and 1:3) and evaluated their electrochemical performances in Li–S batteries. A high sulfur content and crack-free electrode with a loading density of  $10 \text{ mg cm}^{-2}$  was fabricated, as carbon black was substituted by

fine graphite powders. The effect of the volume of electrolyte on the electrochemical performances was also investigated.

## 2. Experimental

C/S composites were prepared by manually mixing carbon black (Denka) or synthetic graphite (KS-6, TIMREX<sup>®</sup>) with precipitated sulfur (99.5%, Alfa Aesar) in different weight ratios in an agate mortar. The mixture of C/S composite (95 wt.%) and poly(vinylidene fluoride) (PVDF, Solef<sup>®</sup> 5130, 5 wt.%) was dispersed in 1-methyl-2-pyrrolidinone (NMP) to form a slurry which was subsequently casted onto Al foil as a current collector. After drying for 2 h in air at 80 °C, electrode discs of 15 mm in diameter were punched out (without pressing) and transferred into an argon-filled glovebox (MBraun) for assembly. The electrolyte used was 1 M lithium bis(tri-fluoromethanesulfonyl)imide (LiTFSI) in solvent mixture of 1,2-Dimethoxyethane (DME) and 1,3-Dioxolane (DOL) (v/v, 1:1) with  $0.725 \text{ mol L}^{-1}$  of lithium nitrate ( $\text{LiNO}_3$ ) as additive. Li–S coin cells (CR2032) were assembled with Li metal as counter electrode. One pair of wave spring and spacer was used to make the cell full-filled. The cathode and Li anode were separated by an Asahi separator with a thickness of 16  $\mu\text{m}$ . The cells were tested on a multi-channel battery tester (Shenzhen Neware Co. Ltd.) at a constant current of 0.1 mA. The cycling voltage range was between 1.5 and 3.2 V (all the voltage mentioned in this work is vs.  $\text{Li}^+/\text{Li}$ ).

## 3. Results and discussion

### 3.1. Optimization of carbon–sulfur ratio

As sulfur exists in its allotrope of octasulfur (cyclo- $\text{S}_8$ ), the  $\text{S}_8$  rings are opened during the discharge and some of the resultant  $\text{S}_8$  chains are further cut shorter. Subsequently, these sulfur with different chain lengths are reduced to a series of  $\text{Li}_2\text{S}_n$  ( $n = 4–8$ ) which are soluble in electrolyte, exhibiting a voltage slope at 2.3 V. Theoretically this step is anticipated to deliver a specific capacity of  $418 \text{ mA h g}^{-1}$ -sulfur; however, in practice the capacity is often affected by incomplete utilization of sulfur, especially if the sulfur particle size is too big. In the followed step, soluble  $\text{Li}_2\text{S}_n$  are further reduced to form insoluble  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  as precipitate on carbon matrix, leading to a long voltage plateau at 2.1 V. This process delivers a theoretical specific capacity of  $1254 \text{ mA h g}^{-1}$ -sulfur. Assuming that sulfur was fully converted into  $\text{Li}_2\text{S}_n$  in the first step, the capacity at the second step should be mainly influenced by the property of the carbon matrix. Generally, larger surface area accommodates more  $\text{Li}_2\text{S}_2$  and  $\text{Li}_2\text{S}$  precipitates, and higher conductivity allows for easier conversion of  $\text{Li}_2\text{S}_2$  to  $\text{Li}_2\text{S}$ . It is noteworthy here that the cycling performance of Li–S batteries can be affected by the nucleation and growth of  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$  [47]. As the cell was further discharged to 1.5 V, another slope at 1.7 V from the reduction of  $\text{LiNO}_3$  appeared [48]. The electrolyte additive,  $\text{LiNO}_3$ , is used to stabilize Li anode by the formation of an enhanced solid electrolyte interface (SEI) film, which can improve the coulombic efficiency of Li–S batteries [49].

As sulfur has poor electronic conductivity, it needs to be blended or combined with a conductive agent, e.g. carbon black, to form C/S composites as working cathode. High sulfur content in the C/S composite favors high energy density; however, too low carbon content will lead to the formation of electrically isolated islands in the electrode. Consequently, the sulfur utilization rate will be low (affecting the capacity delivered at 2.3 V), and so does the subsequent precipitation of soluble  $\text{Li}_2\text{S}_n$  (causing capacity loss at the voltage plateau of 2.1 V). It is thus crucial to have a balanced carbon to sulfur ratio in the C/S composite cathode. As for the carbon sources, some recent work reported carbon black as a good

Download English Version:

<https://daneshyari.com/en/article/7736172>

Download Persian Version:

<https://daneshyari.com/article/7736172>

[Daneshyari.com](https://daneshyari.com)