

Electrochemical performance of sulfur composite cathode materials for rechargeable lithium batteries

Feng Wu^{a,b}, Sheng Xian Wu^a, Ren Jie Chen^{a,b,*}, Shi Chen^{a,b}, Guo Qing Wang^{a,b}

^a School of Chemical Engineering and Environment, Beijing Institute of Technology,

Beijing Key Laboratory of Environmental Science and Engineering, Beijing 100081, China

^b National Development Center for High Technology Green Material, Beijing 100081, China

Received 8 January 2009

Abstract

The structure and characteristic of carbon materials have a direct influence on the electrochemical performance of sulfur–carbon composite electrode materials for lithium–sulfur battery. In this paper, sulfur composite has been synthesized by heating a mixture of elemental sulfur and activated carbon, which is characterized as high specific surface area and microporous structure. The composite, contained 70% sulfur, as cathode in a lithium cell based on organic liquid electrolyte was tested at room temperature. It showed two reduction peaks at 2.05 V and 2.35 V, one oxidation peak at 2.4 V during cyclic voltammogram test. The initial discharge specific capacity was 1180.8 mAh g⁻¹ and the utilization of electrochemically active sulfur was about 70.6% assuming a complete reaction to the product of Li₂S. The specific capacity still kept as high as 720.4 mAh g⁻¹ after 60 cycles retaining 61% of the initial discharge capacity.

© 2009 Ren Jie Chen. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Sulfur composite; Cathode materials; Activated carbon; Electrochemical performance

The lithium–sulfur battery system has almost the highest theoretical capacity of 1672 mAh g⁻¹ and highest theoretical specific energy of 2600 Wh kg⁻¹ of all known cathode materials [1]. Combining with abundant resources, low cost and environmental friendliness of elemental sulfur [2], the lithium–sulfur battery shows great potential for the next generation of high energy density lithium batteries. However, it has been reported that Li–S batteries with organic liquid electrolyte have some problems including low utilization of active material and poor cycle life [3,4]. In order to successfully operate the lithium–sulfur battery, the sulfur cathode material must be well combined with a conductive additive and a strong adsorbent agent [5–7], but the active sulfur content of the composite is comparatively low, which reduced the specific capacity of the composite.

In this paper, we choose activated carbon with large specific surface area and high porous structure in which sulfur particle can be embedded. And the completely airtight heat synthesis method is applied to control the sulfur content of the composite. Owing to its good electrical conductivity and strong absorbability, activated carbon used as matrix to

* Corresponding author at: School of Chemical Engineering and Environment, Beijing Institute of Technology, Beijing Key Laboratory of Environmental Science and Engineering, Beijing 100081, China.

E-mail address: chenrj@bit.edu.cn (R.J. Chen).

embed sulfur can not only improve the conductivity of the sulfur electrode, but can also effectively inhibit the dissolution of sulfur and lithium polysulfides in the liquid electrolyte.

1. Experimental

Activated carbon with BET surface area of $1486 \text{ m}^2 \text{ g}^{-1}$ and average pore diameter of 1.76 nm (taken by NOVA 1200) was mixed with elemental sulfur (100 mesh, Aldrich) by a weight ratio of 3:7. The mixture was kept in a stainless steel airproof jar filled with argon gas. It was heated to $150 \text{ }^\circ\text{C}$ to make elemental sulfur melt and this temperature was kept for 5–8 h for melted sulfur to diffuse into the pores of activated carbon. Then the temperature was enhanced to $300 \text{ }^\circ\text{C}$ and kept for 3–4 h so that the vaporized sulfur was coated onto the surface of the activated carbon. After that, BET surface area of the composite reduced to $2.78 \text{ m}^2 \text{ g}^{-1}$, which indicated that sulfur was well embedded with the pores of activated carbon. Because the weight did not loss during the reaction, the ratio of sulfur was kept at 70% in the composite.

The S–C electrode slurry was made by mixing 70% composite, containing about 49% sulfur and 21% activated carbon, with 20% acetylene black and 10% polyvinylidene fluoride (PVDF) binder in N-methyl-2-pyrrolidinone (NMP) dispersant. Pure sulfur electrode slurry containing 70% sulfur, 20% acetylene black and 10% PVDF was also prepared in the same way to compare with S–C composite electrode. The slurries were spread onto aluminium foil substrates. It was dried in a vacuum oven at $60 \text{ }^\circ\text{C}$ for 24 h. Subsequently, the electrode was cut into disks with a diameter of 11 mm. CR 2025 coin-type cells were assembled in an Ar-filled glove box (M. Braun, Germany) with H_2O and O_2 content below 1 ppm. 1,2-Dimethoxyethane (DME) and 1,3-dioxolane (DOX) (1:1 by vol.) containing 1 mol/L lithium bis(trifluoromethane sulfonyl)imide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI) was used as liquid electrolyte. The cells were galvanostatically discharged and charged in the range of 1.0–3.0 V (vs. Li^+/Li) at a current density of 100 mA g^{-1} with a LAND cyler (Wuhan, China). Cyclic voltammetry (CV) measurements were performed via a CHI 604C electrochemical workstation system (Shanghai, China) at a scanning rate of 0.1 mV s^{-1} . The AC impedance was measured with the fresh cells at open potential. This was also carried out using the CHI 604C electrochemical workstation system. The AC amplitude was $\pm 5 \text{ mV}$. The frequency range applied was 100 kHz to 0.01 Hz.

2. Results and discussion

Fig. 1 shows cyclic voltammogram of the S–C composite electrode. Two reduction peaks were observed and this was due to the multiple reaction mechanisms of sulfur with lithium. The first step could be the transformation of sulfur to lithium polysulfide (Li_2S_n , $8 > n > 2$) at higher potential about 2.35 V, and the second step could be the change of lithium polysulfide to lithium sulfide (Li_2S_2 , Li_2S) at lower potential about 2.05 V [8,9]. One oxidation peak near 2.4 V

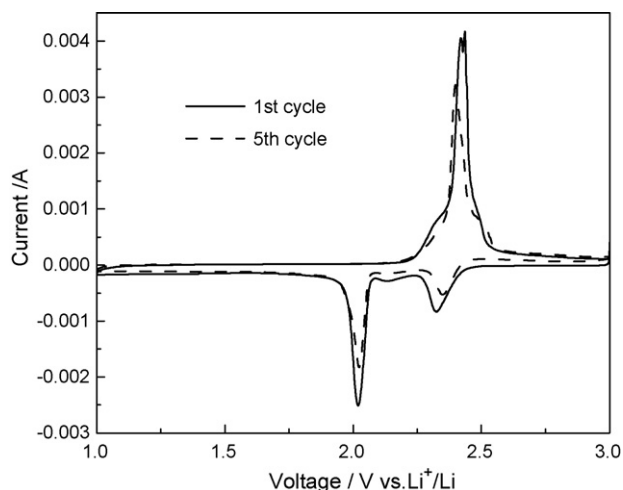


Fig. 1. Cyclic voltammogram curves of the S–C composite electrode at scan rate of 0.1 mV s^{-1} .

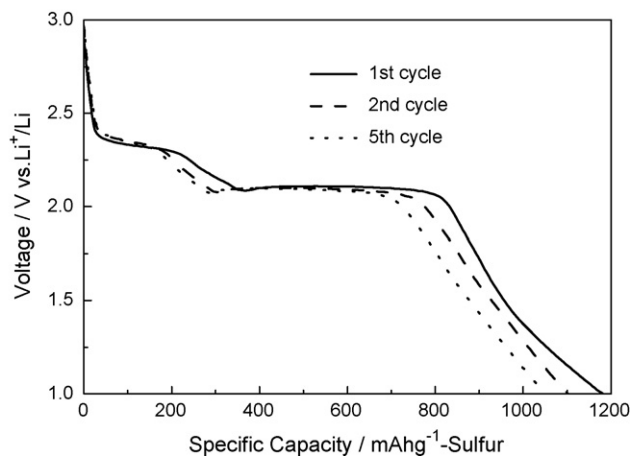


Fig. 2. The discharge profiles for the S–C composite electrode at cut-off potential of 1.0–3.0 V.

is the change to lithium polysulfide (Li_2S_n , $8 > n > 2$). Activated carbon in the composite acts as an electronic conductor and adsorbent, which is electrochemically inert in the potential region used, thus the CV redox peaks are only attributable to the oxidation and reduction of elemental sulfur, no additional peaks were found.

Fig. 2 presents typical discharge curves of the S–C composite electrode in rechargeable lithium cells with organic liquid electrolyte at room temperature. It shows two stable and distinct discharge plateaus: higher discharge plateau at about 2.3 V and lower one at about 2.0 V, which could be assigned to the two step reaction of sulfur with lithium during the discharge process, as demonstrated in the CV measurements. Calculated from the sulfur content, the initial discharge specific capacity of the electrode is about $1180.8 \text{ mAh g}^{-1}$, the utilization of electrochemically active sulfur was about 70.6% assuming a complete reaction to the product of Li_2S .

The cycling performance of the S–C composite electrode is shown in Fig. 3, cycled at a constant current density of 100 mA g^{-1} sulfur. The reversible discharge specific capacity of the composite cathode drops from initial $1180.8 \text{ mAh g}^{-1}$ to 720.4 mAh g^{-1} over 60 cycles with an average fading rate of about 0.6% per cycle which shows a good cyclic stability. The high irreversibility capacity of the first several cycles due to some of the sulfur in the composite which may not embed in the pores of the activated carbon or adsorbed by the activated carbon, this part of the sulfur can dissolve in the liquid electrolyte during the discharge process. The improvement in the capacity and cyclic stability of the cell with the composite electrode could be due to the additive of activated carbon with large specific surface area and high porous structure. Because of its good electrical conductivity and strong absorbability,

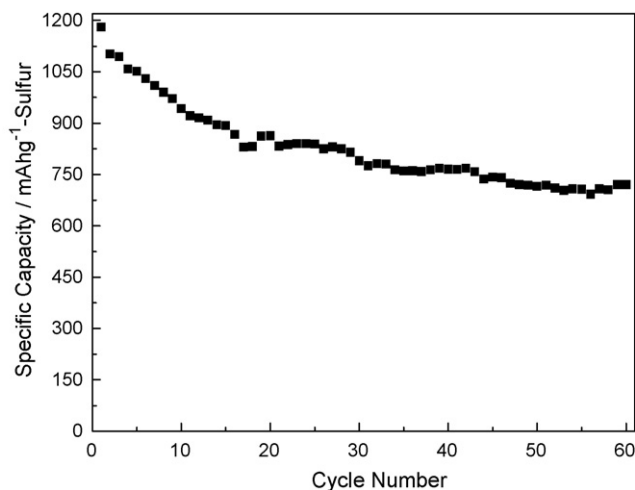


Fig. 3. Cycling performance of the S–C composite electrode at a current density of 100 mA g^{-1} .

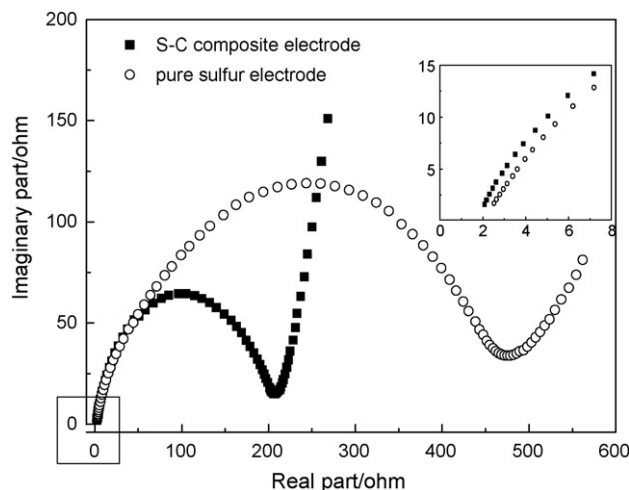


Fig. 4. Impedance plots for the pure sulfur electrode and S–C composite electrode at open potential.

activated carbon not only improves the conductivity of the composite electrode, but also can effectively prevent the sulfur and lithium polysulfides dissolution into the liquid electrolyte.

Fig. 4 contains Nyquist plots of the impedance response measured for the pure sulfur electrode and the S–C composite electrode. The contact resistance between the electrode and electrolyte is showed at the high frequency, and the charge transfer resistance is determined by the diameter of semicircle. It is clear that both the contact resistance and the charge transfer resistance of the composite electrode are smaller than that of the pure sulfur electrode. It can be explained that the composite electrode are homogeneous dispersed composite and more porous than the pure sulfur electrode. Therefore, the high accessibility of the liquid electrolyte to the electrochemically active sulfur particles is easier for the composite electrode. Besides, the activated carbon has good electrical conductivity and can form a dimensional electrical network. Thus the conductivity of the composite electrode is greatly improved and the electrochemical properties of the cell are enhanced.

Acknowledgments

This work was financially supported by the National Key Program for Basic Research of China (No. 2009CB220100) and the National 863 Program (No. 2007AA03Z226).

References

- [1] D. Marmorstein, T.H. Yu, K.A. Striebel, J. Power Sources 89 (2) (2000) 219.
- [2] H. Yamin, E. Peled, J. Power Sources 9 (3) (1983) 281.
- [3] E. Peled, A. Gorenstein, M. Segal, J. Power Sources 26 (1989) 269.
- [4] J. Shim, K.A. Striebel, E.J. Cairns, J. Electrochem. Soc. 149 (10) (2002) 1321.
- [5] J.L. Wang, L. Liu, Z.J. Ling, Electrochim. Acta 48 (13) (2003) 1861.
- [6] W. Zheng, Y.W. Liu, X.G. Hu, Electrochim. Acta 51 (7) (2006) 1330.
- [7] J. Wang, S.Y. Chew, Z.W. Zhao, Carbon 46 (2) (2008) 229.
- [8] B.H. Jeon, J.H. Yeon, K.M. Kim, J. Power Sources 109 (1) (2002) 89.
- [9] H.S. Ryu, H.J. Ahn, K.W. Kim, J. Power Sources 153 (2) (2006) 360.