

Short communication

Electrochemical characteristics of sulfur composite cathode materials in rechargeable lithium batteries

Jiulin Wang*, Yaowu Wang, Xiangming He, Jianguo Ren, Changyin Jiang, Chunrong Wan

Institute of Nuclear Energy Technology (INET), Tsinghua University, Beijing 102201, China

Received 11 May 2004; accepted 5 June 2004

Available online 12 August 2004

Abstract

The charge and discharge characteristics of lithium batteries with sulfur composite cathodes have been investigated. The sulfur composites showed novel electrochemical characteristics. Almost all sulfur in the composites was reduced to Li_2S in the first discharge process and the capacity stabilized at ca. 700 mAh/g and utilization of sulfur corresponded to be above 90%, plus good cyclability. Charged and discharged at relatively high current density, the specific capacity remained above 600 mAh/g and the charge/discharge efficiencies were about 99%. © 2004 Elsevier B.V. All rights reserved.

Keywords: Sulfur cathode; Composite materials; Rechargeable lithium batteries; Cycle performance; Material utilization efficiency

1. Introduction

Elemental sulfur has almost the highest theoretical capacity 1672 mAh/g and theoretical specific energy density 2600 Wh/kg of all known cathode materials for rechargeable lithium batteries. Combined with abundant resources, low cost, sulfur shows great potential as the cathode for the next generation of high performance lithium batteries. Recently, Mikhaylik and Akridge [1] reported that Li/S batteries could work well even at -40°C . Rechargeable lithium batteries using pure elemental sulfur directly as cathode materials (elemental sulfur cathode) encountered some serious problems including low utilization of active material and poor rechargeability, which retarded the application of rechargeable Li/S [2,3]. These difficulties led many researchers to utilize sulfides instead of elemental sulfur, such as DMcT

(2,5-dimercapto-1,3,4-thiadiazole), FeS_2 and CuS , however, these resulted in lower theoretical capacity [4–10].

Low utilization of elemental sulfur and poor charge/discharge performance of Li/S batteries might be due to several factors. It is well known that the discharge products in Li/S batteries are insulating polysulfides Li_2S_x ($1 \leq x \leq 8$). Some of the polysulfide will dissolve in the electrolyte. Besides losing active material, the dissolved polysulfides also deteriorate the conductivity of electrolyte and electrode, leading to quick capacity degradation at high charge and discharge rate [11,12]. On the other hand, part of insulating reaction products cover the sulfur particles and prevent further electrochemical reaction. In our previous papers [13,14], we reported composites with highly dispersed sulfur embedded in the conductive matrix as cathode materials for rechargeable polymer lithium batteries (sulfur composite cathode), which showed novel performances compared to elemental sulfur cathode and effectively overcame the above-mentioned problems.

In this work, we investigated cycle characteristics and rate capability of sulfur composites used as cathode materials for rechargeable lithium batteries.

* Corresponding author. Present address: Department of Chemical Engineering, Center for Automotive materials and manufacturing (CAMM), 945 Princess Street, Kingston, Queen's University, Ont., K7L 5L9 Canada. Tel.: +1 613 547 0116x121; fax: +1 613 547 8125.

E-mail address: wangjl@post.queensu.ca (J. Wang).

2. Experimental

The sulfur composites and gel electrolytes were prepared as reported [14]. A gel electrolyte with ionic conductivity ca. 1.2 mS/cm contained PVDF-HFP copolymer and SiO₂, plus liquid electrolyte EC-DMC-1 M LiPF₆ (Merck, Germany). The composite with sulfur content 45.3 wt.% was mixed with acetylene black and PTFE, using ethanol as dispersant. The weight ratio of the sulfur composite, acetylene black and PTFE in the final dry cathode was 80:15:5. The mixture was rolled into a film with thickness of ca. 100 μm, cut in-to disks with diameter 11 mm and pressed on to nickel foam current collectors. CR2025-type coin cells were assembled in a glove box (M. Braun GmbH, Germany) with H₂O and O₂ content below 1 ppm. A lithium sheet (15 × 0.2 mm) was used as the anode. The charge and discharge performance of the cells was investigated between 1.0 and 3.0 V with a LAND cyler (Wuhan, China) at room temperature.

3. Results and discussion

In the charge/discharge profiles of Li/S batteries with elemental sulfur directly as cathode materials, the reduction process of sulfur contains at least two regions. The first region in the range of 2.4–2.1 V, corresponding to the formation of soluble polysulfides and the second discharge region from 2.1 to 1.5 V, related to the formation of solid reduction product on conductive materials carbon matrix [3,12]. However, using sulfur composites we have reported here as cathode materials, the lithium batteries exhibited different characteristics. There was no obvious voltage region in the charge and discharge curves, almost continuously declining and inclining lines, as reported in our previous papers [13,14]. The first discharge voltage was relatively low with an average value of 1.4 V (based on mid-value of specific capacity). In the following cycles, the average charge and discharge voltages gradually stabilized at 2.19 and 1.83 V, respectively, less than 0.4 V voltage difference between charge and discharge process. Fig. 1 shows the cycle performance of the sulfur composite. The specific capacity was calculated based on the entire composite material. In the first discharge process, the composite showed relatively high specific capacity, up to 807 mAh/g, almost all sulfur in the composite was reduced. The specific capacity stabilized at ca. 700 mAh/g in the following cycles. Take into the consideration of sulfur content and given that polymer matrix was electrochemically inert,

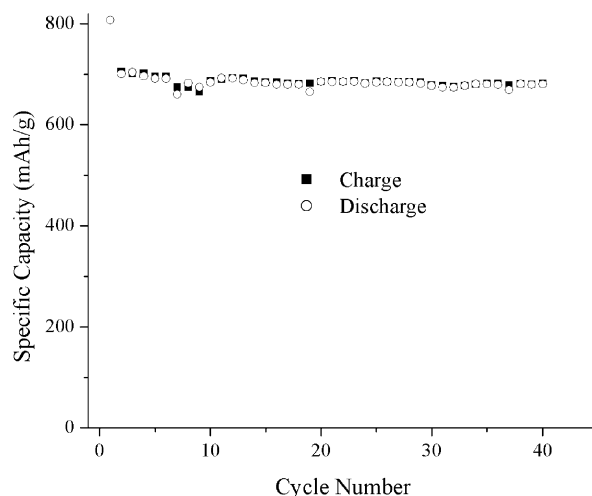


Fig. 1. Cycle performance of lithium battery with sulfur composite cathode.

the specific capacity of sulfur was 1545 mAh/g. Divided by sulfur theoretical capacity 1672 mAh/g, the stable utilization of sulfur was about 92%. After 40 cycles, the specific capacity remained ca. 680 mAh/g. The average capacity degradation rate was only 0.07% per cycle excluding first discharge capacity. It was obvious that the charge and discharge efficiencies of the battery were very high and the efficiencies of all cycles were up to 99% except for the first discharge process, which means that the sulfur in the composite exhibited good electrochemical reversibility via the reaction, $2\text{Li} + \text{S} \leftrightarrow \text{Li}_2\text{S}$.

The results of scanning electron microscopy (SEM) tests indicate that the composites consisted of about 200 nm aggregated particles. Analyzed by transmission electron microscopy (TEM) with the resolution 10 nm, the distribution of sulfur was relatively even across the composite particles and the X-ray photoelectron spectroscopy (XPS) patterns of sulfur indicated that sulfur existed in an elemental state in the composites [14]. The particle sizes of sulfur in the composites were several nanometers or less. But, in the case of the elemental sulfur cathode materials, there existed the large sulfur particles about 5 μm [12], even sulfur “islands” as reported by Cairns [15]. Generally, fine particle materials with large surface area would exhibit high electrochemical activity and good reversibility. Sulfur embedded in the polymer matrix of a nanometer scale, or even molecular level, exhibited high specific capacity via reversible reaction $2\text{Li} + \text{S} \leftrightarrow \text{Li}_2\text{S}$. There might exist strong interactions between the polymer matrix and sulfur particles, which prevent sulfur and

Table 1

Charge and discharge profiles of lithium battery with composite cathode at different current density

Current density (mA/cm ²)	Discharge capacity (mAh/g)	Sulfur utilization (100%)	Average charge voltage (V)	Average discharge voltage (V)
0.5	670.8	88.6	2.219	1.889
1	652.3	86.1	2.272	1.849
1.5	639.6	84.4	2.307	1.81
2	616.9	81.4	2.358	1.775

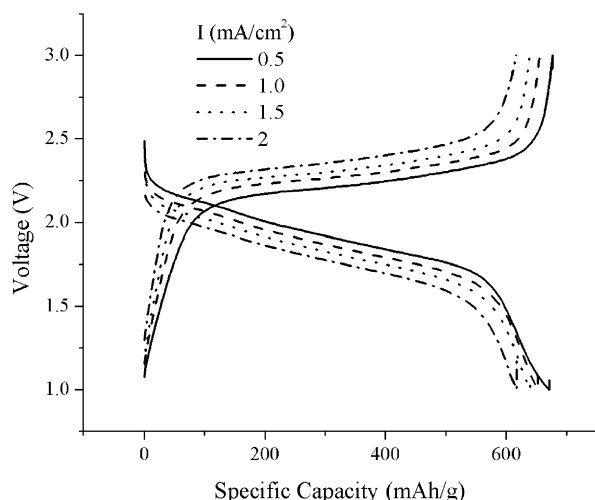


Fig. 2. Effect of current density on lithium battery with sulfur composite cathode.

its product polysulfides from dissolving into the electrolyte, leading to excellent cyclability. Relatively low discharge voltage in the first discharge process might be also attributed to that strong interaction.

Fig. 2 and Table 1 show the charge and discharge profiles of a lithium battery at different current densities. The cells were charged and discharged for three cycles at each current density. The sulfur utilization decreased along with the increase of current density, as shown in Table 1. The difference between average charge voltage and discharge voltage expanded at high current density. It should be noted that the average discharge voltage almost linearly decreased when the current increased, which might mean the internal resistance was a major factor causing specific capacity decreasing at high current density. The charge and discharge efficiencies at different current density are shown in Fig. 3. All efficiencies were around 99%. At higher current density, there were large efficiency value vibrations, which might be caused by lithium dendrites. It was unavoidable that traces of sulfur and poly-

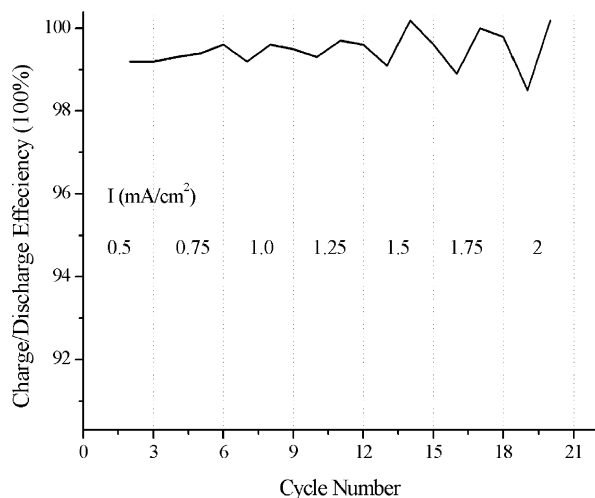


Fig. 3. Charge and discharge efficiencies at different current density.

sulfides would dissolve into the electrolyte and diffuse onto the surface of lithium, which might improve the performance of lithium metal anode, similar to sulfide additives in carbon anodes [16,17]. It was obvious that, even at high current density, sulfur composite cathodes still exhibited high specific capacity, above 600 mAh/g. Moreover, when the current density was small, 0.2 mA/cm², charge and discharge curves and specific capacity recovered initial characteristics.

4. Conclusions

The electrochemical performance of a sulfur cathode could be considerably improved through designing sulfur composite materials. The sulfur composite with the structure of sulfur embedded in the polymer matrix, at nano or even molecular levels, exhibited novel electrochemical characteristics. Almost all sulfur could be reduced via the reaction $2\text{Li} + \text{S} \leftrightarrow \text{Li}_2\text{S}$ and above 90% of sulfur exhibited good electrochemical reversibility, with high charge and discharge efficiency. The composites also possess good high rate performance, even charged and discharged at the current density of 2 mA/cm², the specific capacity remained above 600 mAh/g. Additionally, in the case of elemental sulfur cathode, the dissolving of polysulfides into electrolyte would deteriorate the performance of Li/S batteries, which require an optimized polymer electrolyte [3]. The sulfur composite we report here exhibited good performance even with liquid electrolyte [14].

References

- [1] Y.V. Mikhaylik, J.R. Akridge, *J. Electrochem. Soc.* 150 (2003) A306–A311.
- [2] N. Petr, M. Klaus, K.S.V. Santhanam, H. Otto, *Chem. Rev.* 97 (1997) 265–269.
- [3] D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, *J. Power Sources* 89 (2000) 219–226.
- [4] M.M. Doeff, S.J. Visco, L.C. DeJonghe, *J. Electrochem. Soc.* 139 (1992) 1808–1812.
- [5] N. Oyama, T. Tatsume, T. Sato, T. Sotomura, *Nature* 373 (1995) 598–600.
- [6] F. Matsumoto, M. Ozaki, Y. Inatomi, S.C. Paulson, N. Oyama, *Langmuir* 15 (1999) 857–865.
- [7] P. Wang, *J. Electrochem. Soc.* 149 (2002) A1171–1174.
- [8] S.H. Yang, S. Osmialowski, Q.C. Horn, *J. Electrochem. Soc.* 149 (2002) A1499–1502.
- [9] E. Strauss, D. Golodnitsky, E. Peled, *Electrochem. Acta* 45 (2000) 1519–1525.
- [10] J.S. Chung, H.J. Sohn, *J. Power Sources* 108 (2002) 226–231.
- [11] S.E. Cheon, K.S. Ko, J.H. Cho, S.W. Kim, E.Y. Chin, H.T. Kim, *J. Electrochem. Soc.* 150 (2003) A796–799.
- [12] S.E. Cheon, K.S. Ko, J.H. Cho, S.W. Kim, E.Y. Chin, H.T. Kim, *J. Electrochem. Soc.* 150 (2003) A800–805.
- [13] J.L. Wang, J. Yang, J.Y. Xie, N.X. Xu, *Adv. Mater.* 14 (2002) 963–965.
- [14] J.L. Wang, J. Yang, C.R. Wan, K. Du, J.Y. Xie, N.X. Xu, *Adv. Funct. Mater.* 13 (2003) 487–492.
- [15] E.J. Cairns, <http://www.eande.lbl.gov/BERC/ejc.rep.html>.
- [16] G. Hong, T. Esthers, US Patent 6013394 (2000).
- [17] J.O. Benshenhard, M.W. Wagner, M. Winter, *J. Power Sources* 44 (1993) 413–420.