Short communication

Expansion and shrinkage of the sulfur composite electrode in rechargeable lithium batteries

Xiangming He*, Jianguo Ren, Li Wang, Weihua Pu, Changyin Jiang, Chunrong Wan

Institute of Nuclear & New Energy Technology, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

ABSTRACT

The expansion and shrinkage characteristics of sulfur composite cathode electrode in rechargeable lithium batteries have been investigated. It was found that the sulfur composites electrodes expanded when discharging and shrank when charging again. The thickness change of the electrode was measured to be about 22%. The thickness of lithium metal anodes was also changed when lithium deposition and dissolution, while the sulfur composites electrodes expanded and shrank conversely. The investigation showed that the thickness changes of lithium anode and sulfur composite cathode could be compensated with each other to keep the total thickness of the cell not to change so much.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The sulfur-based cathode materials are attractive for lithium batteries due to their large specific capacity, abundant resources and low cost, showing great potential for the next generation of high-performance lithium batteries [1–4].

Recently, Wang et al. [5–12] reported that the sulfur composites, which were prepared by sulfurization of polyacrylonitrile with elemental sulfur, showed novel performances compared to elemental sulfur cathode and effectively overcame the problems occurring in sulfur electrodes. The sulfur composite presented high specific capacity over $800\,\mathrm{mA\,h\,g^{-1}}$ and excellent cycleability [5–16], showing that the sulfur composite was an alternative promising candidate cathode material for high-performance cells. The prototype polymer cell with the sulfur composite cathode material presented the energy density of $246\,\mathrm{W\,h\,kg^{-1}}$ and $401\,\mathrm{W\,h\,L^{-1}}$ [14]. The rate capability of the sulfur composites and the cycle characteristics at different temperatures were investigated for rechargeable lithium cells [13,15], demonstrating that the lithium cells with the sulfur composite cathodes can be operated above $-20\,^{\circ}\mathrm{C}$ and at a high current density. The discharge capacity of the sulfur composite cathode material increased as the temperature increase from -30 to $60\,^{\circ}\mathrm{C}$. It presented the discharge capacity of 854 and $632\,\mathrm{mA\,h\,g^{-1}}$ at 60 and $-20\,^{\circ}\mathrm{C}$, respectively. The discharge capacity of the sul-

fur composite cathode material decreases as the current density increase. It presents the discharge capacity of 792 and $604\,\mathrm{mA\,h\,g^{-1}}$ at the current density of 55.6 and $667\,\mathrm{mA\,g^{-1}}$, respectively. The novel charge and discharge characteristics of lithium cells with sulfur composite cathodes was revealed [14], showing that the sulfur composite presented two discharge voltage plateaus of 2.10 and 1.88 V, and two charge voltage plateaus of 2.22 and 2.36 V, *via.* Li$^+$/Li. The overcharge tests demonstrated that the sulfur composite had the intrinsic safety for overcharge of lithium cells. The sulfur composite had good reversible capacity after it was deeply discharged even to 0 V. It showed stable cycleability and high cycling capacity of $1000\,\mathrm{mA\,h\,g^{-1}}$ when cycling between 0.1 and 3.0 V.

In addition, the lithium ion batteries are found to be structurally and dimensionally dynamic [17]. The batteries generally expand during charge and contract during discharge. This thickness, thus volume, change is caused by lithium ion intercalation into host materials, i.e. graphite and lithium transition metal oxide and resultant lattice expansion and contraction [18–22]. Expansion of carbon materials is observed to be much more significant than lithium cobalt oxide (LiCoO$_2$) [20]. For carbons, the degree of expansion greatly varies depending on the structure. For example, natural graphite shows almost three times greater volume change than MCMB [23–25]. Quantitatively about 10% increase [18]. The expansion characteristic of the electrode is of important factor for the battery assembly. However, volume change of the sulfur composite during cycling is still unknown. In this study, the expansion and shrinkage characteristics of the sulfur composite electrode was primarily investigated.

* Corresponding author. Tel.: +86 10 89796073; fax: +86 10 89796031.
E-mail addresses: hexm@tsinghua.edu.cn,
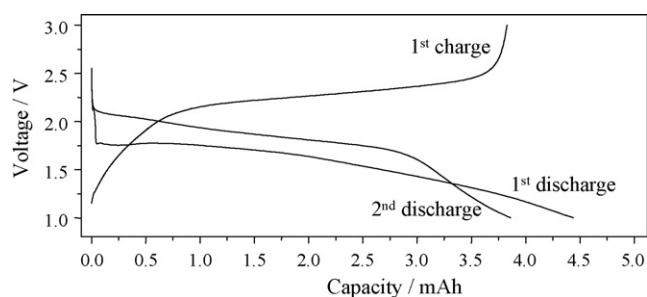hexiangming@tsinghua.org.cn (X. He).

Fig. 1. Discharge/charge curves of the sulfur composite electrode.

2. Experimental

The sulfur composites were prepared as reported [1–3]. The composite with sulfur content 40 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 about 150 μm, cut into Ø10 disks and pressed on to an aluminum collector. The electrodes were then dried at 120 °C under vacuum for 24 h. The plastic packaged cells were assembled in a glove box (M. Braun GmbH, Germany) with H_2O and O_2 content below 1 ppm. A lithium foil was used as the anode and separated by a Celgard 2400 microporous film. The electrolyte was 1.0 M $LiPF_6$ dissolved in a mixture of ethylene carbonate and diethyl carbonate (1:1, v/v). The charge and discharge performance of the cells was tested at room temperature. The normal charge procedure was composed of a constant-current of 0.25 mA cm^{-2}. The normal discharge procedure was composed of a constant-current of 0.25 mA cm^{-2} until the voltage dropped to 1.0 V. The cell was rested for 1 h before it began to be discharged. The cell was opened and the thickness of the sulfur composite cathode was measured at the full charge or discharge state. The measurement was conducted by micrometer. The measurements were performed without mechanical constraint.

3. Results and discussion

The measurements of the electrode thickness are carried out as follows: 30 batteries are assembled and divided into 3 groups. Each group has 10 batteries, for which the measurements of the electrode thickness are conducted in parallel. The average value is obtained from the 10 measurements and the error is about 2% for

the thickness measurement by micrometer. The standard deviations are around 2.

The batteries in group 1 are discharged down to 1 V, and opened for the measurement. The batteries in group 2 are discharged down to 1 V, then charged to 3 V, and opened for the measurement. The batteries in group 3 are discharged down to 1 V, then charged to 3 V, finally discharged down to 1 V again and opened for the measurement. Through above measurements, the electrode thickness change is revealed during charge/discharge cycle. The discharge/charge curves of the sulfur composite electrode are shown in Fig. 1.

The measurements are listed in Table 1. The batteries in group 1 are discharged down to 1 V, delivering an average discharge capacity of 4.48 mA h; the thickness of the cathode changes from an average value of 142 μm to an average value of 173 μm, increasing about 22%. The batteries in group 2 are discharged down to 1 V, and then charged to 3 V, presenting an average charge capacity of 3.81 mA h; the thickness of the cathode changes to an average value of 149 μm, increasing about 4% from the initial state. The batteries in group 3 are discharged down to 1 V, then charged to 3 V, finally discharged down to 1 V again, delivering an average 2nd discharge capacity of 3.81 mA h; the thickness of the cathode changes to an average value of 169 μm, increasing about 19% from the initial state.

The above measurements indicate that the sulfur composite cathode expands from 142 to 173 μm thick after intercalation of 4.48 mA h lithium ion into the cathode, and shrinks down to 149 mm thick after de-intercalation of 3.81 mA h lithium ion from the cathode, and then expands to 169-μm thick after intercalation of 3.81 mA h lithium ion into the cathode again. In above process, the anode of lithium foil is calculated to decrease by 29.5 μm after dissolution of 4.48 mA h lithium ion from lithium foil, and to increase by 25.1 μm after deposition of 3.81 mA h lithium ion on the lithium foil, and then to decrease by 25.1 μm after dissolution of 3.81 mA h lithium ion from the lithium foil again. The calculation is based on 3865 mA h g^{-1} capacity of lithium, 0.5 g cm^{-3} density of lithium foil and Ø10 disc of the electrode. The thickness changes of both anode and cathode during charge and discharge are summarized in Table 2. The results show that the sulfur composites electrode expands when discharging (lithium ion intercalation) and shrinks when charging (lithium ion de-intercalation) again. The thickness of lithium metal anodes is also changed when lithium deposition and dissolution, while the sulfur composites electrodes expands and shrink conversely.

Fig. 2 illustrates the expansion and shrinkage of the sulfur composite electrode in rechargeable lithium batteries. The

Table 1
The capacity and thickness of the sulfur composite electrode during cycling

Sample	Initial cathode thickness (μm)	1st discharge		1st charge		2nd discharge	
		Capacity (mA h)	Thickness (μm)	Capacity (mA h)	Thickness (μm)	Capacity (mA h)	Thickness (μm)
Group 1	142	4.48	173				
Group 2	143	4.48		3.81	149		
Group 3	143	4.48		3.81		3.81	169

Note: the value is average one obtained from the 10 measurements and the error is about 2% for the thickness measurement by micrometer.

Table 2
Summary of expansion and shrinkage of the sulfur composite electrode during cycling

Sample	Initial cathode thickness (μm)	1st discharge		1st charge		2nd discharge	
		Thickness (μm)	Thickness change (μm)	Thickness (μm)	Thickness change (μm)	Thickness (μm)	Thickness change (μm)
Cathode	143	173	+30	150	−23	169	+19
Anode	160		−29.5		+25.1		−25.1

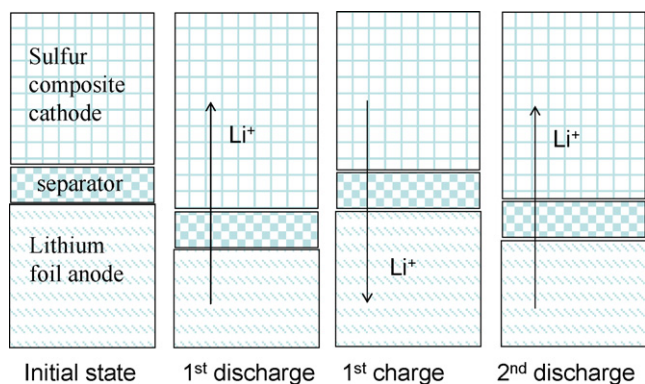*Note*: the thickness of the anode (lithium foil) is calculated by the capacity of charge or discharge.

Fig. 2. Sketch of the expansion and shrinkage of the sulfur composite electrode in rechargeable lithium batteries.

sulfur composite cathode expands during discharge, while the anode shrinks because of the lithium dissolution, resulting in the movement of the separator. The sulfur composite cathode shrinks during charge, while the anode expands because of the lithium deposition, resulting in the movement of the separator in opposite direction. The investigation shows that the thickness changes of lithium anode and sulfur composite cathode can be compensated with each other to keep the total thickness of the cell not to change so much. Although the thickness of the cell shows little change during cycling, the thickness changes of the sulfur composite and the compensation from the opposite change of lithium anode can lead to the movement of the separator. The movement of the separator would causes the capacity fading of the cell which is assembled by coiling technique. However, it causes less capacity fading of the cell which is assembled by stacking technique.

4. Conclusions

This study has revealed that the sulfur composites electrodes expanded when discharging and shrank when charging. The thickness change of the electrode was measured to be about 22%. The thickness of lithium metal anodes were also changed when lithium deposition and dissolution. The investigation showed that the thickness changes of lithium anode and sulfur composite cathode could be compensated with each other to keep the total thickness of the cell not to change so much.

References

[1] N. Petr, M. Klaus, K.S.V. Santhanam, H. Otto, Chem. Rev. 97 (1997) 265–269.
[2] D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, J. Power Sources 89 (2000) 219–226.
[3] 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.
[4] 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.
[5] J.L. Wang, L. Liu, Z.J. Ling, J. Yang, C.R. Wan, C.Y. Jiang, Electrochim. Acta 48 (13) (2003) 1861.
[6] J.L. Wang, J. Yang, C.R. Wan, K. Du, J.Y. Xie, N.X. Xu, Adv. Func. Mater. 13 (6) (2003) 487.
[7] J.L. Wang, J. Yang, J.Y. Xie, N.X. Xu, Adv. Mater. 14 (13-14) (2002) 963.
[8] J.L. Wang, J. Yang, J.Y. Xie, N.X. Xu, Y. Li, Electrochem. Commun. 4 (6) (2002) 499.
[9] J. Yang, B.F. Wang, K. Wang, Y. Liu, J.Y. Xie, Z.S. Wen, Electrochem. Solid State Lett. 6 (8) (2003) A154.
[10] X.G. Yu, J.Y. Xie, J. Yang, H.J. Huang, K. Wang, Z.S. Wen, J. Electroanal. Chem. 573 (1) (2004) 121.
[11] X.G. Yu, J.Y. Xie, J. Yang, K. Wang, J. Power Sources 132 (1–2) (2004) 181.
[12] X.U. Yu, J.Y. Xie, Y. Li, H.J. Huang, C.Y. Lai, K. Wang, J. Power Sources 146 (1–2) (2005) 335.
[13] J.L. Wang, Y.W. Wang, X.M. He, J.G. Ren, C.Y. Jiang, C.R. Wan, J. Power Sources 138 (1–2) (2004) 271.
[14] X.M. He, W.H. Pu, J.G. Ren, L. Wang, J.L. Wang, C.Y. Jiang, C.R. Wan, Electrochim. Acta 52 (2007) 7372.
[15] X.M. He, W.H. Pu, J.G. Ren, L. Wang, J.L. Wang, C.Y. Jiang, C.R. Wan, Ionics 14 (2008) 335–337.
[16] W.H. Pu, X.M. He, L. Wang, Z. Tian, C.Y. Jiang, C.R. Wan, Ionics 13 (2007) 273.
[17] J.H. Lee, H.M. Lee, S. Ahn, J. Power Sources 119–121 (2003) 833.
[18] T. Ohzuku, Y. Iwakoshi, K. Sawai, J. Electrochem. Soc. 140 (1993) 2490.
[19] K. Sawai, Y. Iwakoshi, T. Ohzuku, Solid State Ionics 69 (1994) 273.
[20] J.N. Reimers, J.R. Dahn, J. Electrochem. Soc. 139 (1992) 2091.
[21] E. Buiel, J.R. Dahn, Electrochim. Acta 45 (1999) 121.
[22] J.R. Dahn, A.K. Sleigh, H. Shi, J.N. Reimers, Q. Zhong, B.M. Way, Electrochim. Acta 38 (1993) 1179.
[23] M. Majima, T. Tada, S. Ujiie, E. Yagasaki, S. Inazawa, K. Miyazaki, J. Power Sources 81–82 (1999) 877.
[24] T. Ohzuku, N. Matoba, K. Sawai, J. Power Sources 97–98 (2001) 73.
[25] M. Majima, K. Hanafusa, Y. Oka, G. Tanaka, H. Yoshida, E. Yagasaki, T. Tada, J. Power Sources 68 (1997) 448.