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Charge/discharge characteristics of sulfur composite cathode materials in rechargeable lithium batteries

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Abstract

The charge and discharge characteristics of lithium batteries with sulfur composite cathodes have been investigated. The sulfur composites showed novel electrochemical characteristics. The analysis of the differential capacity indicated that the discharge process showed two voltage plateaus of 2.10 V and 1.88 V, and the charge process also presented two voltage plateaus of 2.22 V and 2.36 V. The overcharge test showed that the composite cannot be charged over 4.0 V, the voltage always stopped at about 3.9 V during charging, indicating that the composite presented the intrinsic safety for the overcharge of lithium batteries. The overcharge can cause serious safety problem for the conventional Li-ion batteries. The overcharge test also showed that the batteries with sulfur composite were destroyed when the upper cut-off voltage was over 3.6 V. However, the composite presented good reversible capacity after it was deep discharged even to 0 V. It showed stable cycleability and high cycling capacity of 1000 mAh g^{-1} when cycling between 0.1 V and 3.0 V, indicative of the different characteristic from the conventional oxide cathode materials. The prototype polymer battery with the composite cathode material presented the energy density of 246 Wh kg^{-1} and 401 Wh L^{-1}.

Keywords: Sulfur composite cathode materials; Rechargeable lithium batteries; Electrochemical characteristics; Deep discharge; Overcharge; Safety

1. Introduction

Elemental sulfur has almost the highest theoretical capacity 1672 mAh g^{-1} and theoretical specific energy density 2600 Wh kg^{-1} 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, It was reported that lithium–sulfur (Li–S) cells with liquid electrolytes had critical drawback in the aspects of cycle life, rate capability, and sulfur utilization [1,2]. 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/discharge rate [3,4]. On the other hand, part of insulating reaction products cover the sulfur particles and prevent further electrochemical reaction. Wang et al. [5–12] 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. The cycle characteristics and rate capability of sulfur composites cathode materials was investigated for rechargeable lithium batteries [13]. In this study, novel charge and discharge characteristics of lithium batteries with sulfur composite cathodes were reported, including deep discharge and overcharge characteristics, and charge/discharge voltage plateaus.

2. Experimental

The sulfur composites were prepared as reported [5–7]. The components of the composite are: 1.2 wt.% H, 15.8 wt.% N, 41.2 wt.% C and 41.8 wt.% S. The composite was mixed with acetylene black and PTFE, using ethanol as dispersant. The

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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. The electrodes were then dried at 120 °C under vacuum for 24 h. CR2025-type coin 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 with a LAND cycler (Wuhan, China) at room temperature. The normal charge procedure was composed of a constant-current of 0.25 mA cm^{-2} followed by constant-voltage at 3.0 V until the current tapered down to 0.025 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.

Fig. 2. Prototype polymer battery with sulfur composite cathode.

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 polysulfide and the second discharge region from 2.1 V to 1.5 V, related to the formation of solid reduction product on conductive materials carbon matrix [2,4]. It was reported that the lithium batteries using sulfur composites as cathode materials exhibited different characteristics. There was no obvious voltage region in the charge and discharge curves, almost continuously declining and inclining lines, as reported in Refs. [6,7]. As shown in Fig. 1a, the first discharge voltage of sulfur composite is relatively low with an average value of 1.5 V (based on mid-value of specific capacity). In the following cycles, the average charge and discharge voltages gradually stabilize at 2.24 V and 1.95 V, respectively, less than 0.3 V voltage difference between charge and discharge process, the discharge (charge) curves are similar after 1st discharge. Fig. 1b shows the cycling performance of sulfur composite. In the first discharge process, the sulfur composite shows relatively high specific capacity, up to 967 mAh g^{-1}. The specific capacities stabilize at ca. 800 mAh g^{-1} in the following cycles. After 30 cycles, the specific capacity remains ca. 758 mAh g^{-1}. The average capacity degradation rate is less than 0.2% per cycle excluding first discharge capacity. It is obvious that the charge and discharge efficiencies of the battery are very high and the efficiencies of all cycles are up to 100% except for the first discharge process, which means that the sulfur composite exhibits good electrochemical reversibility.

The prototype polymer battery with sulfur composite cathode in the size of 4 mm × 40 mm × 26 mm was assembled, as shown in Fig. 2. It presents the energy density of 246 Wh kg^{-1} and 401 Wh L^{-1}, showing higher energy density than the conventional $LiCoO_2$ battery, which energy density is about 180 Wh kg^{-1}.

The differential capacity curves (dQ/dV) curves can be used to elucidate some of the locations of lithium storage in active materials [14–20]. The differential capacity curves permit easy graphical analysis. Phenomenological speaking, the peaks in the differential capacity curves represent equilibrium of electrochemical reaction, where the reactions of electrochemical reduction/oxidation of the cathode material take place. It was reported that there was no obvious voltage plateaus in the charge/discharge curves of sulfur composite, almost continuously declining and inclining lines [6,7,13]. Apparently, the charge and discharge curves present no voltage plateaus, as shown in Fig. 1. However, in the differential discharging capacity profile (Fig. 3a) derived from the discharge voltage profile, two separate peaks at 2.10 V and 1.88 V indicate that the sulfur

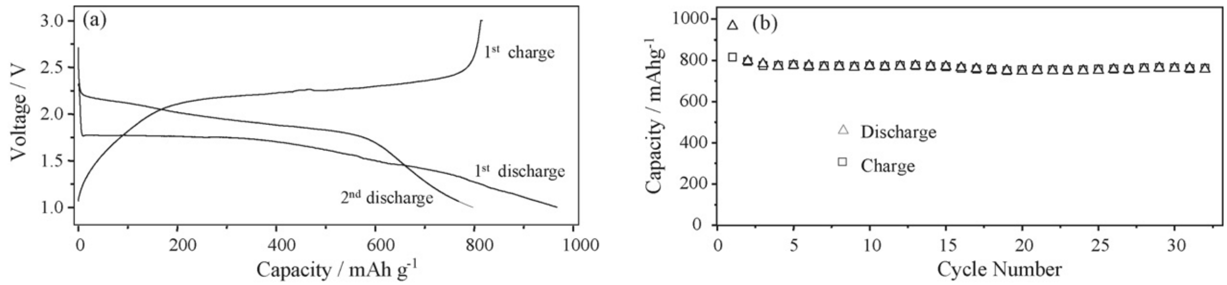

Fig. 1. Charge/discharge of lithium battery with sulfur composite cathode between 3.0 and 1.0. (a) 1st discharge, 1st charge and 2nd discharge, the discharge (charge) curves are similar after 1st discharge. (b) Cycleability.