

Short communication

Self-discharge of lithium–sulfur cells using stainless-steel current-collectors

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Abstract

The self-discharge behaviour of Li–S cell, is investigated through changes in the open-circuit voltage (OCV) and discharge capacity with storage time. A fresh Li–S cell experiences 72% sulfur utilization during the first discharge, as based on the theoretical capacity for the formation of Li₂S. After 30 days of storage, the OCV has fallen from 2.48 to 2.16 V and the discharge capacity has decreased from 1206 to 924 mAh g⁻¹ (based on sulfur). Analysis of the self-discharged sample by a variety of techniques shows the formation of lithium polysulfides, such as Li₂S_n ($n \geq 1$) from the reaction of lithium and sulfur, which is related to the corrosion of the stainless current-collector. Stainless steel is not the most appropriate current-collector material for Li–S cells. The extent of self-discharge can be decreased by using a gold-coated current-collector that offers protection against corrosion.

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1. Introduction

Lithium batteries are now widely used as power sources for mobile devices such as portable televisions, cellular phones, and laptop computers. Sulfur is a very attractive active material for cathodes in lithium batteries because of its high theoretical specific capacity, i.e., 1675 mAh g⁻¹ based on sulfur [1]. Following the report by Cairns et al. [2] that a Li–S cell is feasible, many researchers have been trying to make a version with high utilization and long cycle-life. Some researchers have constructed Li–S cells using electrolytes containing lithium polysulfides [3–5]. Because of the insulating nature of sulfur and the solubility of polysulfides in the organic electrolytes, only low utilization of the active material and poor cycleability were obtained. Chu [6] was awarded a patent relating to a Li/PEO/S cell which showed

above 80% utilization of sulfur and 30 charge–discharge cycles. Shin et al. [7] reported a high discharge capacity of over 1200 mAh g⁻¹ (based on sulfur) for a Li–S cell that used a polyvinylidene fluoride gel electrolyte at room temperature. The cycling properties of Li–S cells have been improved by protection of the lithium metal anode [8] or addition of carbon nanotubes [9]. Some researchers have investigated the electrochemical properties at sub-zero temperatures [10], room temperature [11,12], and elevated temperature [13,14]. Self-discharge behaviour is one of the important factors for commercialization of lithium batteries [16,17], but there have been no reports of the self-discharge of Li–S cells.

Accordingly, the present study addresses this parameter by measurement of the open-circuit voltage (OCV) and the discharge capacity of a Li–S cell with a stainless-steel current-collector. The self-discharge mechanism is investigated by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD) analysis, and scanning electron microscopy (SEM).

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2. Experimental details

2.1. Preparation of sulfur cathode

Elemental sulfur powder (–200 mesh, 99.98%, Aldrich), poly ethylene oxide (PEO, $M_w = 4 \times 10^6$, Aldrich) and acetylene black carbon (AB, Aldrich) were dried at 70, 50 or 130 °C for 24 h under vacuum. The mixture was milled in an attrition mill, and then acetonitrile (99.5%, Junsei Chemical Co.) was added. The slurry was cast on to a glass plate and dried in air at room temperature, and then in a vacuum at 50 °C for 12 h. The sulfur electrode was composed of 50 wt.% elemental sulfur powder, 30 wt.% carbon, and 20 wt.% PEO.

2.2. Preparation of electrolyte

A copolymer of vinylidene fluoride and hexafluoropropylene (PVdF-co-HFP; Kynar 2801, Atochem) and lithium trifluoromethane sulfonate (LiCF_3SO_3 , Aldrich Co.) were dried for 24 h under vacuum at 90 and 130 °C, respectively. Tetra ethyleneglycol dimethylether (TEGDME, Aldrich Co.) and tetrahydrofuran (THF) were used as received. The PVdF copolymer was completely dissolved in THF. Then the liquid electrolyte (TEGDME and LiCF_3SO_3) was added to the polymer solution and the mixed solution was further stirred. The amount of liquid electrolyte was 200 wt.% of the matrix polymer, which is sufficient to retain the mechanical strength of the polymer electrolyte. After complete homogenization of the mixture, the resulting viscous solution was cast on a glass plate and allowed to dry in a glove box at room temperature. The dried film was then removed from the substrate and used as a polymer electrolyte. All the preparations were conducted in a glove box purged with argon.

2.3. Preparation of cell and electrical property measurements

The Li–S cell was assembled by stacking the plasticized polymer electrolyte between a sulfur cathode and a lithium anode, as shown schematically in Fig. 1. Type 316 stainless steel was used as the current-collector in each electrode. The cell was finally packaged with swage fitting. In order to study the self-discharge behaviour of the Li–S cell, the changes in the OCV and capacity were measured as a function of storage time. The cell was typically discharged to 1.7 V at a constant specific current of 100 mA g^{-1} (based on sulfur) at room temperature with a WBCS3000 (WonA Tech. Co.) test station.

2.4. Analysis of sulfur electrode

The thermal stability and crystalline structure of the sulfur electrode were examined by means of DSC (TA Instrument Inc.) and XRD (Rekagu) analysis, respectively. Surface morphologies were observed with SEM (JEOL Co.). All the preparations were conducted in a glove box purged with ar-

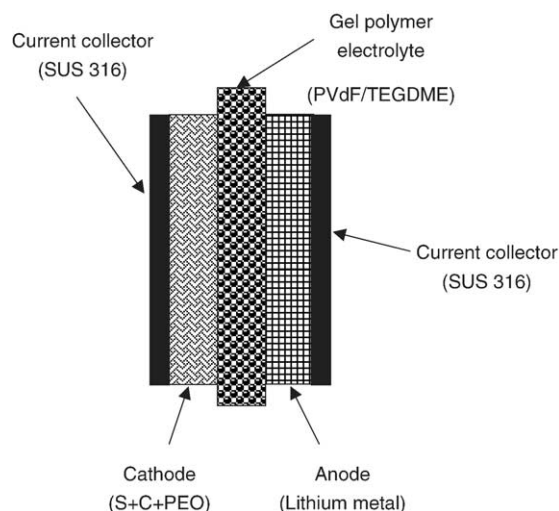


Fig. 1. Schematic diagram of Li–S cell with stainless-steel current-collector.

gon. The DSC pan could be sealed in an argon atmosphere and thus protected from contamination by air.

3. Results and discussion

The change in the OCV of the Li–S cell with storage time after assembly are shown Fig. 2. The OCV falls abruptly from 2.48 to 2.21 V after 7 days, and then decreases very slowly. The difference in standard reduction potential between lithium and sulfur is 2.57 V, which coincides with the standard electrode potential difference.

The change in the discharge curve with storage time is presented in Fig. 3. The original Li–S cell displays two plateau regions, which should be related to the two reduction steps of sulfur. These observations coincide with previous results [7,15]. It was suggested that the upper plateau region might correspond to the formation of lithium polysulfides by the reduction of elemental sulfur, and the low plateau region to the formation of lithium sulfide (Li_2S) by reduction of lithium polysulfides [15]. The discharge capacity was 1206 mAh g^{-1} (based on sulfur) which corresponds to about 72% utilization

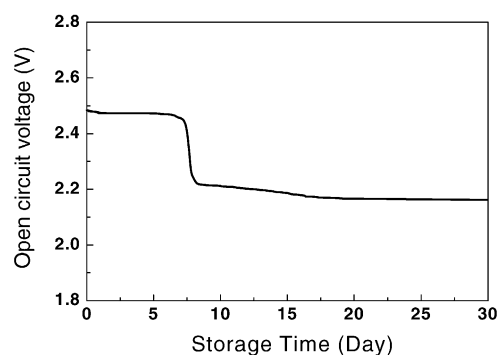


Fig. 2. Changes in OCV of Li–S cell with storage time.

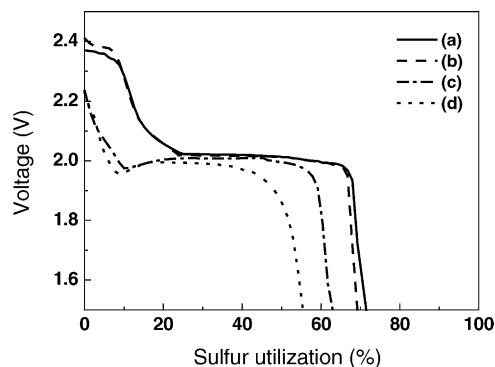


Fig. 3. Changes in discharge profiles as function of storage time: (a) original cell, (b) 3 days, (c) 10 days and (d) 30 days.

based on the formation of Li_2S . As the storage time increases, the discharge capacity gradually decreases. After 3 days, the discharge curve is almost the same as the initial one. After 10 days storage, the cell shows only the lower plateau region. The disappearance of the upper plateau results from the decrease of the OCV to 2.2 V. The discharge capacity gradually decreases, and the cell suffers 17% self-discharge after 30 days at room temperature. In order to determine the origin of the self-discharge, the cell materials were characterized by various techniques after various storage times.

Electron micrographs of the sulfur electrode are given in Fig. 4. The fresh electrode consists of a uniform mixture of small particles of carbon or sulfur. After 30 days storage, it

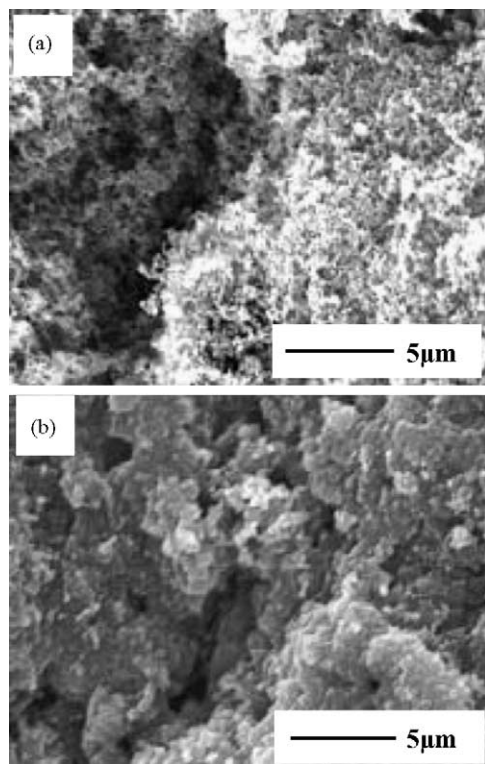


Fig. 4. Electron micrographs of sulfur electrode by: (a) original sample and (b) after 30 days storage.

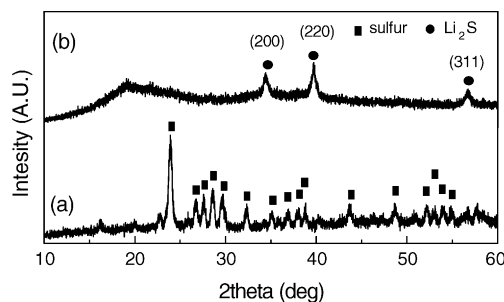


Fig. 5. Changes in XRD pattern of sulfur electrode: (a) original sample and (b) after 30 days of storage.

changes to a smooth surface with agglomeration of the small particles.

X-ray diffraction patterns for the sulfur electrode as a function of storage time are given in Fig. 5. The original sulfur electrode has the orthorhombic structure of sulfur. After 30 days storage, there are no traces of the sulfur peak, but new peaks have appeared that correspond to Li_2S .

The DSC curves for the sulfur electrode at various storage times are presented in Fig. 6. The original sulfur electrode has two endothermic peaks, which are related to elemental sulfur [18]. The endothermic peaks disappear after 30 days of storage, which indicates the disappearance of elemental sulfur. During self-discharge, the sulfur is changed to Li_2S . After 30 days of storage, the OCV of the Li–S cell decreases from 2.48 to 2.16 V, and the discharge capacity decreases to 17% of the original value. The elemental sulfur in the sulfur electrode is changed to Li_2S . From the above results, it is possible to conclude that the decrease in discharge capacity results from the formation of Li_2S . If all of the elemental sulfur is changed to Li_2S , the Li–S cell should have no discharge capacity, and the OCV should be much below 2.2, however e.g., 0 V. The cell has two reduction steps such as formation of lithium polysulfides ($\text{Li}_2\text{S}_n, n > 1$) and Li_2S . The above experimental results can be explained by the partial formation of lithium polysulfides ($\text{Li}_2\text{S}_n, n > 1$), which cannot be detected by XRD. The rapid fall in OCV and the disappearance of the upper plateau can be related to the formation of lithium polysulfides ($\text{Li}_2\text{S}_n, n > 1$) from elemental sulfur and

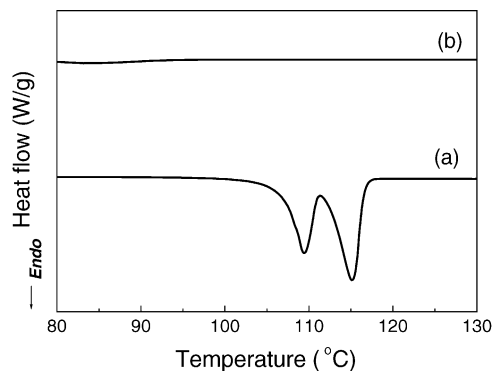


Fig. 6. Changes in DSC curves of sulfur electrode: (a) original sample and (b) after 30 days of storage.

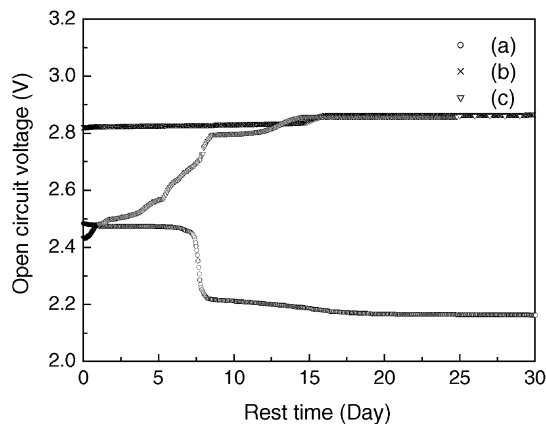
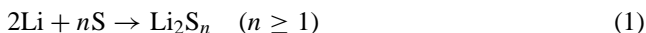


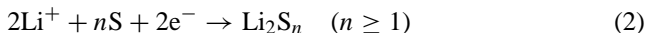
Fig. 7. Changes in OCV of Li-S cell with storage time under various conditions using: (a) PVdF electrolytes with lithium salt (LiCF_3SO_3), (b) PVdF electrolytes without lithium salt and (c) gold-coated stainless-steel current-collector.

lithium. The loss in discharge capacity can result from the formation of lithium polysulfides (Li_2S_n , $n > 1$) and Li_2S as in Eq. (1), which is similar to the normal discharge process



whereas the sulfur originates from the elemental sulfur of the sulfur cathode, the lithium can come from either the lithium ions (Li^+) of LiCF_3SO_3 in the electrolyte, or from the elemental lithium of the lithium anode. In order to identify the source of lithium, a Li-S cell was assembled with PVdF gel electrolyte, that did not contain any lithium salt such as LiCF_3SO_3 .

The OCV of the cell is about 2.8 V and does not change for 30 days see Fig. 7. This is very different behaviour from that exhibited by the cell using lithium salt. Thus, the lithium may come from the lithium salt, which can be easily ionised in the electrolyte. During self-discharge, the lithium involved might in the form of lithium ions (Li^+). In order to react with lithium ions, the elemental sulfur should also be ionised, i.e., by accepting electron from other sources:



Jow and coworkers [17] explained that the self-discharge of a Li-ion battery is related to corrosion of the aluminum substrate. Traces of pitting corrosion of the stainless-steel current-collector have been found in the present study. Thus, the electrons in the above reaction can be imported from the corrosion of stainless steel via in the following equation:



It should be noted, however, that iron ions (Fe^{2+}) or iron compounds have not been detected. This requires further study. In order to prevent corrosion of the current-collector, the stainless-steel substrate was coated with gold using the sputtering method. The OCV was 2.43 V and increased to 2.83 V, which is similar to that for the cell using PVdF gel electrolyte without lithium salt. In other words, a decrease in OCV could

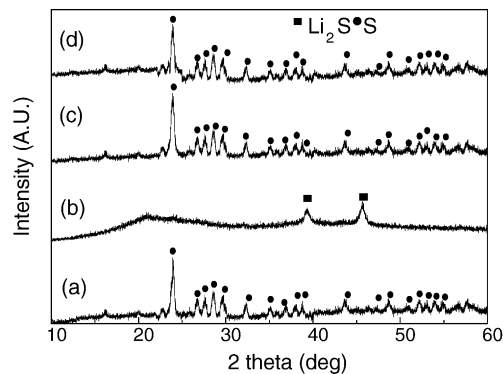
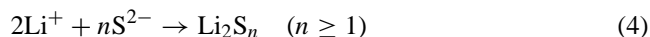


Fig. 8. XRD pattern of sulfur electrode under various conditions: (a) original sample, (b) 30 days stored sulfur electrode using PVdF electrolyte with lithium salt, (c) 30 days stored sulfur electrode using PVdF electrolyte without lithium salt and (d) 30 days stored sulfur electrode using gold-coated stainless-steel current-collector.

not be observed when using a gold-coated current-collector or a PVdF electrolyte without lithium salts.

The changes in the X-ray diffraction pattern for various sulfur electrodes after 30 days storage are given in Fig. 8. For the Li-S cell with a PVdF gel electrolyte without lithium salt, there are no structural changes in the sulfur electrode such as the formation of lithium sulfides. Thus, the self-discharge of a Li-S cell using a stainless current-collector is caused by the formation of lithium sulfides from the reaction of lithium and sulfur ions, which is related to the corrosion of the stainless-steel current-collector as indicated by Eq. (3), i.e.,



The overall reaction that involves the corrosion of the stainless steel and the formation of lithium polysulfides can be represented by:



4. Conclusions

A Li-S cell with stainless-steel current-collectors exhibits severe self-discharge behaviour. After 30 days of storage, the OCV has dropped from 2.5 to 2.2 V and the discharge capacity has a decreased to 72% of the original capacity. Analysis of the self-discharged sulfur electrodes by SEM, XRD, and DSC reveals the formation of lithium polysulfides such as Li_2S_n ($n \geq 1$). It is concluded that polysulfides are formed from the lithium and sulfur ions, and are which are linked to the corrosion of the stainless-steel current-collector. Stainless steel is not an appropriate material for use as the current-collector for the sulfur electrode in the Li-S cell. The self-discharge rate of the Li-S cell can be decreased by using a gold-coated current-collector, which can provide corrosion resistance.

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