

Short communication

## Discharge process of Li/PVdF/S cells at room temperature

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### Abstract

The Li/PVdF/S cell showed the first discharge capacity of  $1268 \text{ mAh g}^{-1}$ , which was about 78% utilization of theoretical value. There were two plateau regions at the first discharge curve. From the XRD, DSC results of the sulfur electrode, elemental sulfur disappeared at the upper plateau region and  $\text{Li}_2\text{S}$  was formed at the low plateau region. We suggested the discharge process of Li/polymer electrolyte/S cell. The elemental sulfur changed into  $\text{Li}_2\text{S}_n$  ( $n > 4$ ) and subsequently changed into  $\text{Li}_2\text{S}$  at a lower plateau potential region.

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### 1. Introduction

There has been a strong incentive to develop a high specific energy battery for portable electronic devices and electric vehicles. Elemental sulfur is very attractive cathode material of lithium battery because of high theoretical capacity,  $1672 \text{ mAh g}^{-1}$  and low material cost [1]. Cairns et al. [2] reported the possibility of Li/S cell assembly. Peled et al. [3] constructed Li/S cell using organic electrolytes containing lithium polysulfides. Because of insulating nature of sulfur ( $5 \times 10^{-30} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ ) and solubility of lithium sulfides in organic electrolytes, they obtained very low utilization of active material and poor cycle property [3,4]. Recently, Chu [5] issued a patent [5] of the Li/S cell showing above 60% utilization of theoretical specific energy. Many researches have been performed in this field since this patent. Marmorstein et al. [6] showed the effect of various polymer electrolytes on the electrochemical property of Li/S cell. The discharge properties of Li/S cell using liquid electrolyte were reported at various temperatures, such as sub-zero [7], room temperature [8–12] and elevated temperature [13,14]. And also, cycling

property of Li/S cell has been improved by protection of lithium metal anode [15] or addition of carbon nanotube [16]. Cheon et al. [17] explained that sulfur changed to lithium polysulfide ( $\text{S} \rightarrow \text{Li}_2\text{S}_n \rightarrow \text{Li}_2\text{S}$ ) during discharge process of Li/S cell with liquid organic electrolyte. However, there were only a few studies on the Li/S cell with gel polymer electrolyte, which could have good mechanical property. Especially, the poly(vinylidene difluoride-co-hexafluoropropylene (PVdF-co-HFP) gel polymer electrolyte with tetra ethylene glycol dimethylether (TEGDME) had good mechanical property and high ionic conductivity. Shin et al. [18] reported high discharge capacity over  $1200 \text{ mAh g}^{-1}$  using Li/S cell with PVdF-co-HFP gel electrolyte at room temperature. There was no study on the discharge mechanism of Li/S cell using polymer electrolyte.

In this study, we investigated the discharge process of Li/S with PVdF gel polymer electrolyte using scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and X-ray diffractometer (XRD).

### 2. Experiment

Elemental sulfur powder ( $-200$  mesh, 99.98%, Aldrich), poly(ethylene oxide) (PEO,  $M_w 4 \times 10^6$ , Aldrich) and acety-

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lene carbon black carbon (Aldrich) were dried at 80 °C, 50 °C and 120 °C for 24 h under vacuum, respectively. The acetonitrile poured into the mixed powder of sulfur, PEO and carbon and then stirred for 24 h to make homogeneous slurry. The slurry was cast onto a glass plate and dried in air at room temperature and then in a vacuum at 50 °C for 12 h. The sulfur electrode film had about 50 μm thickness, 1.54 cm<sup>2</sup> area, 2.2 mg weight and the composition of 60 wt.% elemental sulfur powder, 25 wt.% carbon and 15 wt.% PEO. The PVdF gel polymer electrolyte was prepared from 0.5 M LiCF<sub>3</sub>SO<sub>3</sub>, tetraglyme as plasticizer, 5.5% Kynar 2801 and a gelling agent (PVdF powder) in THF solvent in an argon filled glove box. The amount of plasticizer was 200 wt.% of PVDF as the matrix polymer, which is enough to retain the mechanical strength of the polymer electrolyte. The mixed slurry was heated for 1 h at 60 °C and then poured into a glass dish. A freestanding PVdF electrolyte film was obtained after solvent was evaporated in the glove box at room temperature. Li/PVdF/S cells were assembled in the stainless-steel cell holders made from Swagelock union with polypropylene ferrules. The discharge and charge of cell were carried out using WonA tech cyler regime of constant specific current (100 mA g<sup>-1</sup>) to cut-off voltages of 1.7 V and 3.5 V at room temperature (22 °C).

In order to examine the morphology changes of sulfur electrode during discharge process, SEM (JEOL JSM-6400) was used. The changes of elemental sulfur at sulfur electrode was examined using DSC (DSC2010, TA Instrument) and X-ray diffractometer.

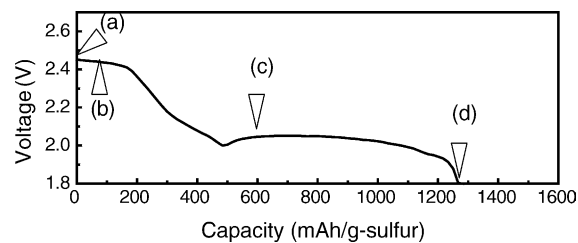


Fig. 1. The first discharge curve of Li/PVdF/S cell and the sulfur electrode samples during discharge reaction process: (a) original, (b) 6% (100 mAh g<sup>-1</sup>) discharge, (c) 36% (600 mAh g<sup>-1</sup>) discharge and (d) 72% (1268 mAh g<sup>-1</sup>) discharge.

### 3. Results and discussion

Fig. 1 shows the first discharge curve of Li/PVdF/S cell at room temperature. The Li/S cell had two plateau potential regions. The upper plateau potential was 2.45 V and the lower plateau region (2.05 V) started from 30% utilization of theoretical capacity, i.e. 500 mAh g<sup>-1</sup>. This result was very similar as previous one of Li/S cell using PEO electrolyte [13,14], liquid electrolyte [8–10]. Two plateau regions were considered as two different reduction steps of sulfur during discharge process. Li/PVdF/S with TEGDME showed the capacity of 1268 mAh g<sup>-1</sup> of active sulfur, which was about 78% utilization of theoretical value. In order to investigate the discharge mechanism, we prepared the sulfur electrode sample marked arrows, such as (a) original, (b) 6% (100 mAh g<sup>-1</sup>) discharged at the upper plateau region, (c) 36% (600 mAh g<sup>-1</sup>) discharged at the lower plateau region

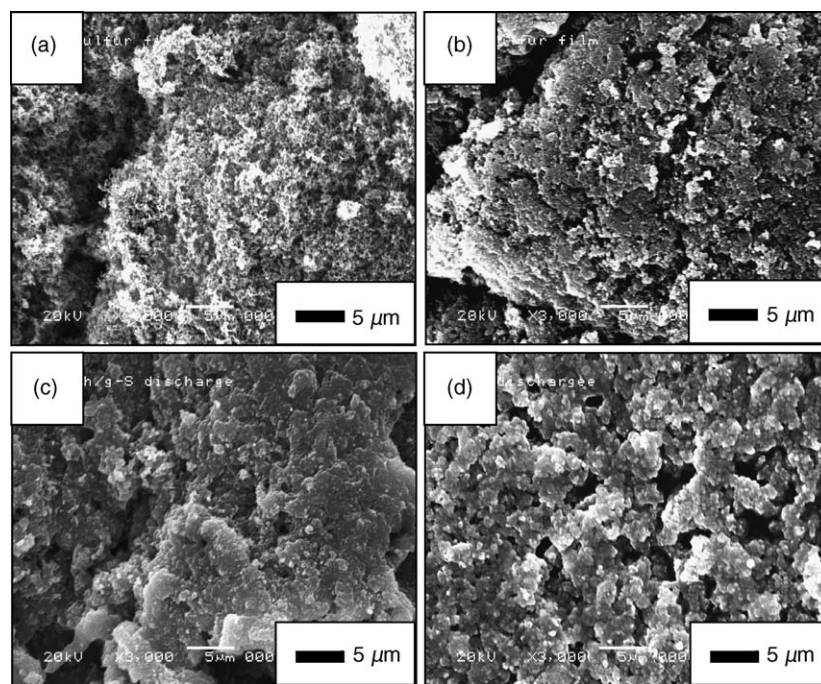


Fig. 2. The SEM morphologies of sulfur electrode as a function of discharge process: (a) original, (b) 6% (100 mAh g<sup>-1</sup>) discharge, (c) 36% (600 mAh g<sup>-1</sup>) discharge and (d) 72% (1268 mAh g<sup>-1</sup>) discharge.

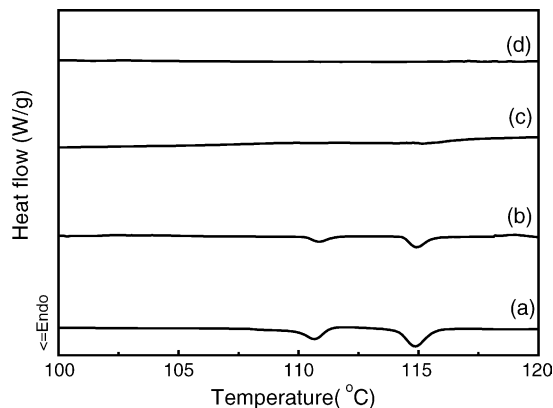


Fig. 3. The changes of DSC curves of sulfur electrode during discharge process: (a) original, (b) 6% ( $100 \text{ mAh g}^{-1}$ ) discharge, (c) 36% ( $600 \text{ mAh g}^{-1}$ ) discharge and (d) 72% ( $1268 \text{ mAh g}^{-1}$ ) discharge.

and (d) 72% ( $1268 \text{ mAh g}^{-1}$ ) discharged electrode. Fig. 2 shows the SEM morphologies of sulfur electrode as a function of discharge process. The original sulfur electrode represented homogenous mixing of sulfur, carbon and PEO. Full discharged sulfur electrode (d) showed bunch shape of small particles, which might be related to agglomerate of components. Fig. 3 represents the changes of DSC curves of sulfur electrode during discharge process. The original sulfur electrode (a) had two endothermic peaks from  $100^\circ\text{C}$  to  $120^\circ\text{C}$ , which came from the melting of elemental sulfur [1,19]. The peak area decreased after 6% discharge of theoretical capacity (b). The peak area represented the amount of heat of melting, which related to amount of elemental sulfur. Thus, the amount of elemental sulfur decreased during discharge at the upper plateau region (b). At the lower plateau region (c) and full discharged sample (d), we could not find out any traces of endothermic peaks of elemental sulfur, which should indicate no existence of elemental sulfur in the sulfur electrode.

The changes of XRD pattern are shown in Fig. 4. The original sulfur electrode (a) had orthorhombic structure, which was stable crystalline structure of elemental sulfur. The peak area of sulfur drastically decreased at the upper plateau region

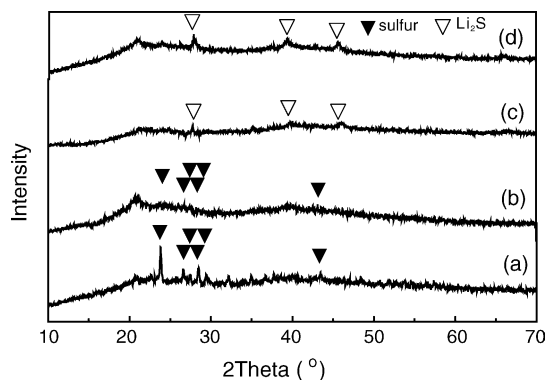


Fig. 4. The XRD pattern of sulfur electrode during discharge process: (a) original, (b) 6% ( $100 \text{ mAh g}^{-1}$ ) discharge, (c) 36% ( $600 \text{ mAh g}^{-1}$ ) discharge and (d) 72% ( $1268 \text{ mAh g}^{-1}$ ) discharge.

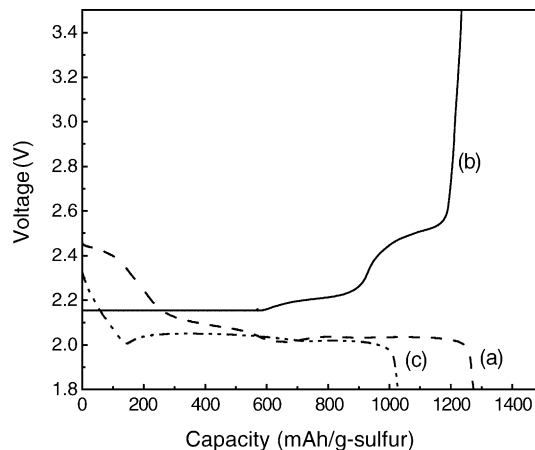


Fig. 5. The discharge-charge curves of lithium/PVdF/sulfur cell: (a) first discharge curve, (b) first charge curve and (c) second discharge curve.

(b). At the lower plateau region (c), we could find out new peaks which were coincided with  $\text{Li}_2\text{S}$ . For the full discharged sample (d), the X-ray diffraction peak area of  $\text{Li}_2\text{S}$  increased, which was related to increasing amount of  $\text{Li}_2\text{S}$ .

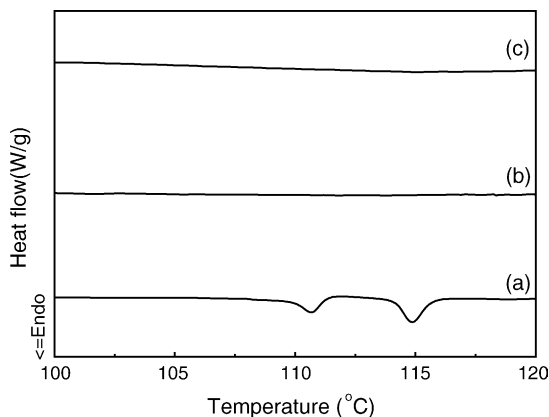


Fig. 6. The changes of DSC curves during discharging-charging: (a) original sulfur electrode, (b) first discharge and (c) first charge.

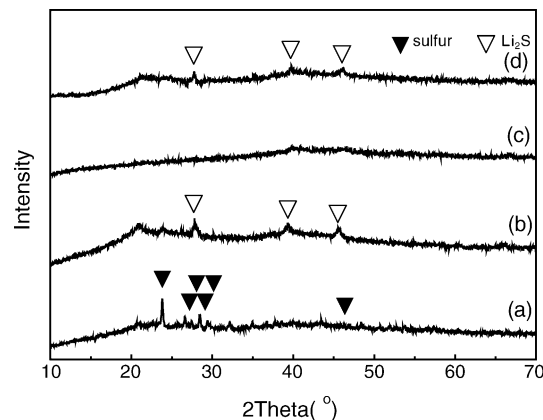


Fig. 7. The changes of XRD pattern during discharging-charging: (a) original sulfur electrode, (b) first discharge, (c) first charge and (d) second discharge.

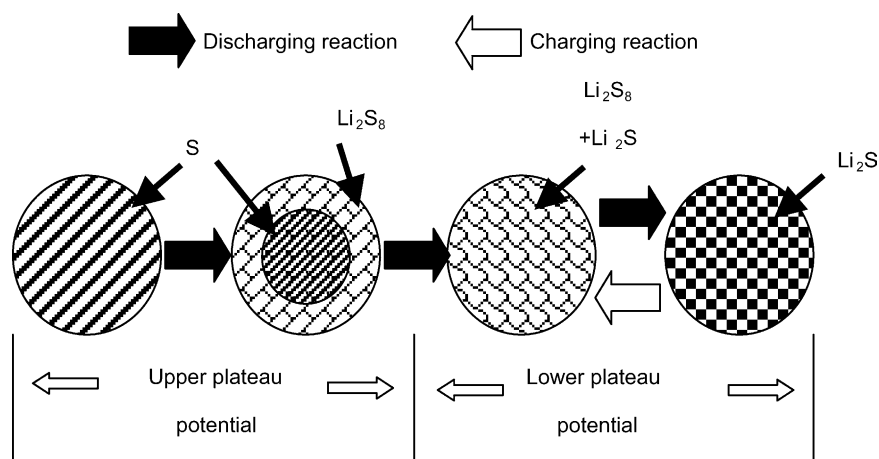
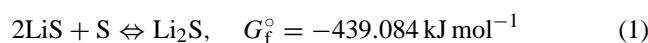


Fig. 8. The discharge and charge reaction model of lithium/sulfur cell.

From the data of XRD and DSC, we could suggest the discharge reaction process of lithium/polymer electrolyte/sulfur cell. From the stable phase diagram [20], the stable compound between sulfur and lithium is  $\text{Li}_2\text{S}$ . Considering thermodynamic aspects of equation (1), the theoretical open circuit voltage is 2.27 V [21].



The low plateau 2.05 V region could be explained using the formation of  $\text{Li}_2\text{S}$ , however, higher plateau 2.4 V region could not explain the formation of  $\text{Li}_2\text{S}$ . This was coincided with the previous experimental DSC, XRD results. Hemmingsem [22] reported that the theoretical open circuit potential (OCP) of polysulfide,  $\text{Li}_2\text{S}_n$  ( $n > 1$ ) was higher than  $\text{Li}_2\text{S}$ . The high potential plateau might be related with the formation of  $\text{Li}_2\text{S}_n$  ( $n > 1$ ). And also, Cheon et al. [17] explained that  $\text{Li}_2\text{S}_n$  would be formed first in the upper plateau region and then  $\text{Li}_2\text{S}$  would be formed. From the DSC and XRD results, all of elemental sulfur changed to lithium polysulfides at the upper plateau region, and there was no elemental sulfur at lower plateau region.

Fig. 5 shows the discharge–charge curves of Li/S cell at room temperature. The second discharge curve showed the capacity decrease from  $1268 \text{ mAh g}^{-1}$  to  $1028 \text{ mAh g}^{-1}$ , and disappearance of upper plateau region. In order to investigate the origin of decrease of second discharge capacity, XRD and DSC test were performed. Fig. 6 shows the changes of DSC curves during discharging–charging. The charged sulfur electrode had no endothermic peaks, which was same as full discharged one. In other words, elemental sulfur could not form by charging, which might be related to the disappearance of upper plateau region at second discharge. Fig. 7 shows the XRD pattern changes of sulfur electrode during charge–discharge. The original sulfur electrode showed orthorhombic structure, which was related to elemental sulfur. After first discharge, the elemental sulfur disappeared and  $\text{Li}_2\text{S}$  was formed. For full charged sample, the  $\text{Li}_2\text{S}$  dis-

appeared and also sulfur was not detected. This result was coincided with the DSC. And,  $\text{Li}_2\text{S}$  reappeared after the second discharge. We suggested that reaction (2) occurred at the upper plateau region, and then lower plateau region came from reaction (3). However, complete reverse reaction did not occur during charging.

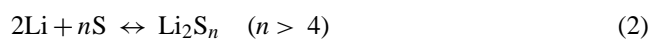


Fig. 8 shows the discharge and charge reaction model of Li/S cell. The elemental sulfur changed to lithium polysulfides at upper plateau region, and polysulfides transformed to  $\text{Li}_2\text{S}$  at the lower plateau region. During charging,  $\text{Li}_2\text{S}$  recovered to lithium polysulfides (reverse reaction of (3)) not elemental sulfur.

#### 4. Conclusion

The Li/S cell using PVdF polymer electrolyte had two plateau potential regions and discharge capacity of  $1268 \text{ mAh g}^{-1}$  at first discharge. The discharge capacity decreased to  $1028 \text{ mAh g}^{-1}$  and the upper plateau region disappeared after second discharge. From the data of XRD, DSC and discharge curves, we could suggest the discharge process of Li/PVdF/S cell at room temperature. The elemental sulfur might be changed into  $\text{Li}_2\text{S}_n$  ( $n > 4$ ) at an upper plateau potential region and  $\text{Li}_2\text{S}_n$  changed into  $\text{Li}_2\text{S}$  at a lower plateau potential region. The elemental sulfur could not recover even after full charge.

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