LI 이차전지용 유황 양극의 방전 전위에 따른 퇴화거동에 관한 연구

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A study on the Capacity Fading Mechanism of Sulfur Cathode Depending on Discharge Potential for Li Rechargeable Battery

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ABSTRACT

유황 양 전극과 액체 전해질, 리튬 금속을 음극으로 사용한 리튬 유황 전지를 제조하여 그 특성을 조사하였다. 유황 전극은 유황파우더와 carbon black 올 도전재로, 그리고 바인더로 PVdF를 사용하여 제조하였다. 이렇게 제조된 셀은 두개의 다른 전압 구간에서 충방전 실험을 행하였다. 첫 번째 셀은 $S_8 + xLi \leftrightarrow Li_2S_x$ (x = 4 ~ 12) 반응만을 일어나게 하기 위하여 2.1V 와 2.5V 사이에서, 그리고 두 번째 셀은 $Li_2S_x + xLi \leftrightarrow Li_2S$ (x = 2 ~ 4)의 반응만을 일어나게 하기 위하여 1.5V 와 2.5V 에서 충방전 하였다. 그 결과 첫 번째 셀이 더 좋은 싸이클 특성을 가지는 것을 확인 할 수 있었다. 각 전압구간에서 각 셀이 충방전 되는 동안, 전해질 내로 녹아난 유황의 양은 큰 차이가 없는 것을 확인하였다. 그리고, 전압에 따른 전극의 임피던스를 측정한 결과, 방전이 끝난 후 큰 저항성분이 새로 생긴 것을 확인 할 수 있었다. 이는 사이클이 진행된 후의 전극표면을 SEM 분석을 행한 결과로부터 사이클이 진행된 후 전극 표면에 최종 반응 산물인 Li_2S 가 피막형태로 형성된 것을 확인 할 수 있었다.

주요기술용어 : Li-S battery(Li-s 전지), Degradation mechanism(퇴화기구), Li_2S film(Li_2S 필름)

1. Introduction

In recent years, there has been an increasing need for high energy density rechargeable batteries for portable electronic equipment. For

the commercialized lithium rechargeable batteries using lithium cobalt (or nickel) oxide or lithium manganese oxide, further increases in battery specific energy have been limited by the extent of lithium intercalation into transition metal oxides, resulting in capacities in the range 100 ~ 150 mAh/g of active material. In contrast, lithium/sulfur (Li-S) secondary battery system is highly attractive power source with high energy density because of the high theoretical specific capacity of sulfur cathode material (approximately 1,675 mAh/g based on active material) and the use of sulfur is advantageous as it is relatively cheap and environmentally benign[1]. Although the Li-S battery has many advantages, A Li-S battery with a 100 % sulfur positive electrode is impossible to discharge at low temperatures because sulfur is known to be an insulator. Therefore, the cathode must be a composite of an electrically conductive material and an ionic conductor well mixed with sulfur[2~4]. Prior studies of Li-S cells with liquid electrolytes had serious problems of low active-material utilization and poor cycle-life, due to the insulating nature of sulfur and Li_2S, and to the loss of active material in the form of soluble polysulfide reaction products. And the incomplete reversibility of the reactions to lower-order sulfides (e.g. Li_2S_2, Li_2S) was also a problem[5~9]. J.H. Shin et al. [10] showed that Li-S cells using a poly(ethylene-oxide)-based composite electrolyte had more than 85 % of the theoretical value of positive electrode at 90 °C. However, capacity fade of Li-S battery is a still persistent problem especially ambient temperature. In this work, we prepared a composite sulfur cathode and investigated its electrochemical properties and attempted to

determine the reasons for the decline of capacity with cycling employing the different charging-discharging potential in a Li-S battery.

2. Experimental

The sulfur electrodes were prepared from a mixture of sulfur (99.98%, Aldrich), carbon black (Acetylene black, as electrical conductor), and polyvinylidene fluoride (PVDF, as binder). The electrode composition for this set of experiments was 30% (w/w) sulfur, 60% (w/w) carbon, and 10 % (w/w) PVDF. The coin type cell(2016) was used to determine the electrochemical characteristics of sulfur electrode. The working electrode was sulfur electrode and the counter electrode was Li foil (~310 µm thick), and the electrolyte was the solution of 1M lithium (bis)trifluoro methanesulfonate imide (LiTFSI, Aldrich) in polyethylene glycol dimethyl ether (PEGDME, Mw 500, Aldrich). The porous polypropylene (Celgard 2400) was used as separator. Cells were assembled inside a glove box filled with argon gas. Cell-cycling tests were carried out on a TOSCAT-3100U (TOYO SYSTEM Co.,LTD.) at 100 µA/cm^2) over the voltage ranges of 3.5~1.5 V, 2.5~ 1.5 V, and 3.5~2.1 V. The impedance measurements were performed over a frequency range of 1 MHz to 1 mHz at AC amplitude of 5 mV with a Solartron 1255-frequency response analyzer. The cyclic voltammetry was performed with a EG&G Potentiostat/Galvanostat Model 273 A. A SEM (Philips XL 30 SFEG) was used for the study of surface topology. The amount of sulfur dissolved into electrolyte with cycling was determined by the sulfur analyzer (SC-432 DR sulfur analyzer).

3. Results and Discussion

The voltage profiles and cyclic behavior of the prepared Li/S cell cycled between 1.5 V and 3.5 V were given in Fig. 1. The highest discharging capacity of the cell was 516 mAh/g. And at 50th cycles, the discharge capacity of this cell is only 394 mAh/g. This poor cyclic behavior is assigned by some reasons. The one reason has been attributed that the active material formed of lithium polysulfides can dissolve in the electrolyte with cycling so active material can be lost in cathode[1,2]. And the other is that the Li_2S, the product of discharging, has poor reversibility. But it is not clear which is major degradation reason and the specific degradation mechanism is still ambiguous. The Li/S cell shows two charging, discharging plateaus respectively. The upper voltage plateaus are caused by following reaction [13].

$$S_8 + xLi^+ \leftrightarrow Li_2S_x \quad (x = 4 \sim 12) \qquad (1)$$
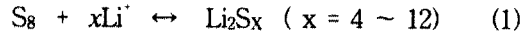
And the lower voltage plateaus are caused by following reaction [13].

$$Li_2S_x + xLi^+ \leftrightarrow Li_2S \quad (x = 2 \sim 4) \qquad (2)$$
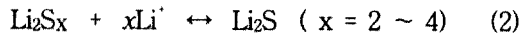
From XRD analyses shown in Fig. 2, it can be known that the sulfur reacts with the Li ion
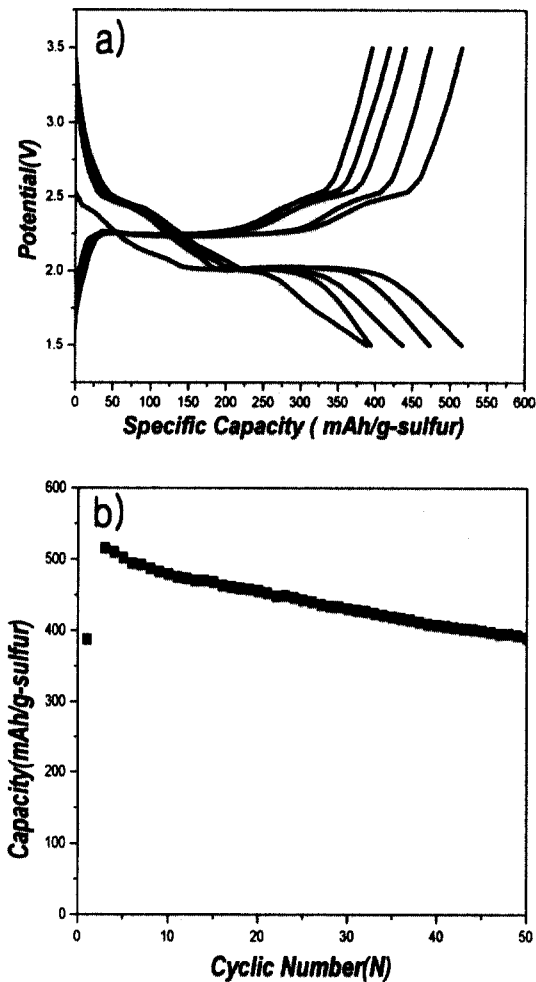

Fig. 1. The voltage profiles (a) and cyclic behavior (b) of the prepared Li/S cell cycled between 1.5 V and 3.5 V.
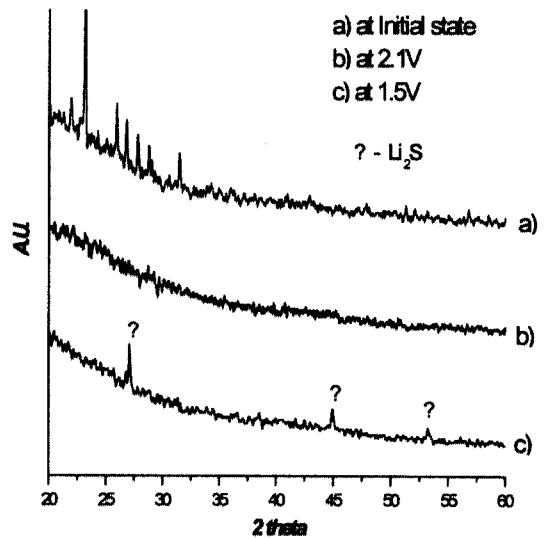

Fig. 2. XRD analyses of sulfur cathode at initial state(a), at 2.1 V(b), and at 1.5 V(c).

and produces lithium polysulfides (Li_2S_x) and finally Li_2S. To know the characteristics of each reaction, one cell was charged and discharged between 2.1 V and 3.5 V and the other was charged and discharged between 1.5 V and 2.5 V. The first was intended to proceed " $S_8 + xLi^+ \leftrightarrow Li_2S_x$ ($x = 4 \sim 12$) " reaction, and the second was intended to proceed " $Li_2S_x + xLi^+ \leftrightarrow Li_2S$ ($x = 2 \sim 4$) " reaction. The charging/discharging profile and cyclic behavior of each reaction were given in Fig. 3 and Fig. 4 respectively.

By making a comparison Fig. 3 and Fig. 4, it can be seen that the lower voltage reaction has larger capacity than the upper voltage reaction but the upper voltage reaction marked (1) has better reversibility than the lower voltage reaction.

From these results, the degradation mechanism of Li/S cell was proposed like this. When the cell is discharged, sulfur reacts with Li ion and produces the lithium polysulfides that can be easily dissolved into electrolyte. Some lithium polysulfides can diffuse out from electrolyte. These lithium polysulfides react further with Li ion and produce the lithium sulfide, Li_2S. But some lithium polysulfides produce the Li_2S on the electrode surface and
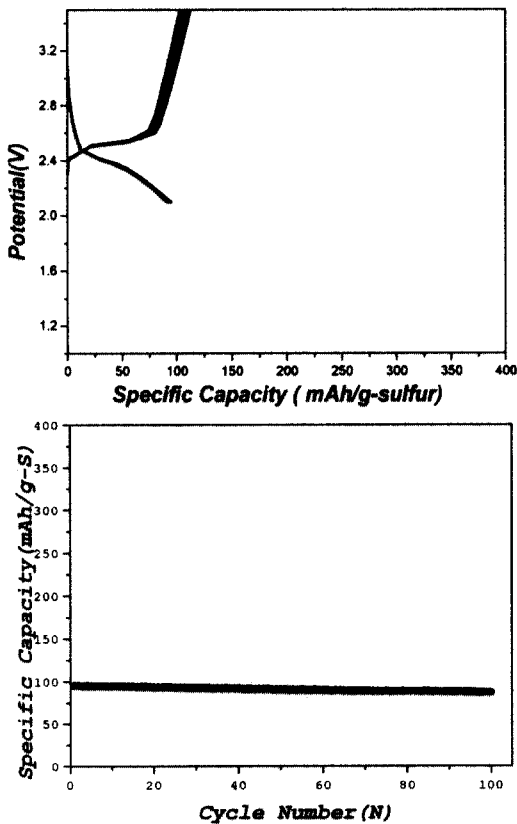

Fig. 3. The charging/discharging profiles and cyclic behavior of the cell cycled between 2.1 V and 3.5 V.
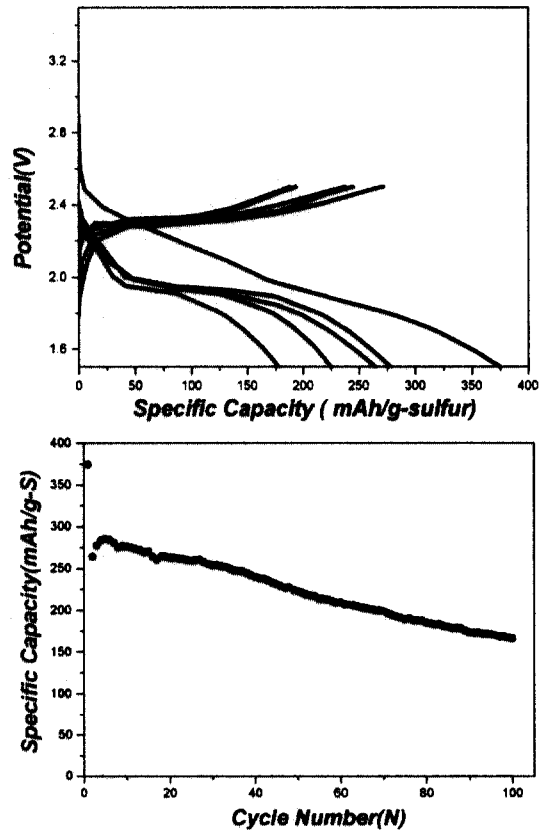

Fig. 4. The charging/discharging profiles and cyclic behavior of the cell cycled between 1.5 V and 2.5 V.
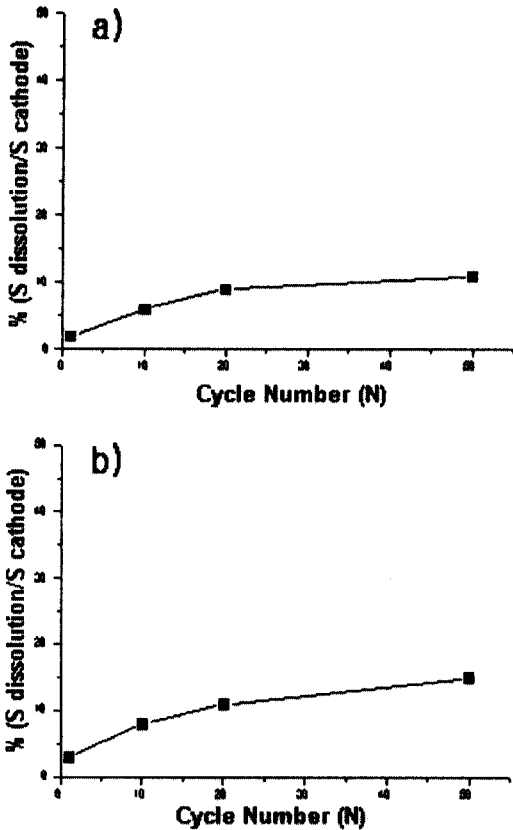
Fig. 5. The amount of sulfur dissolved into the electrolyte with cycling between 2.1 V and 3.5 V (a) and between 1.5 V and 2.5 V (b).

then they disturb the Li ion movement and have poor contact with carbon matrix. So this film increases and becomes thicker with the cell cycling. This may be the main cause of the degradation of the Li/S cell. The lithium polysulfides would dissolve into electrolyte, but if they would not diffuse out to electrode surface, the cycle life of the Li/S cell will be improved. To clarify this result, sulfur dissolution analyses with cycling were performed. Fig. 5a) and Fig. 5b) shows the amount of sulfur dissolved into electrolyte with cycling between each voltage region. When the

cell was cycled between 1.5 V and 2.5 V, the amount of sulfur dissolved into electrolyte was 2, 6, 9, 11 wt% of sulfur cathode at 1, 10, 20, 50 cycle respectively. And when the cell was cycled between 2.1 V and 3.5 V, the amount of sulfur dissolved into electrolyte was 3, 8, 11, 15 wt% of sulfur cathode at 1, 10, 20, 50 cycle respectively. When the cell was cycled between 1.5 V and 2.5 V, the amount of sulfur dissolved into electrolyte was somewhat larger than that of the cell cycled between 2.1 V and 3.5 V. But the difference of the amount of sulfur dissolved into electrolyte is not significant. So it can be concluded that the active material loss into electrolyte is not the fatal factor of the degradation of Li/S cell. Fig. 6 shows the cyclic voltammetry of the Li/S cell. From this cyclic voltammogram, two discrete discharging peaks and a large charging peak were observed. With respect to voltage, electrochemical impedance spectroscopy was performed. Fig. 7a), Fig. 7b) and Fig. 7c) show
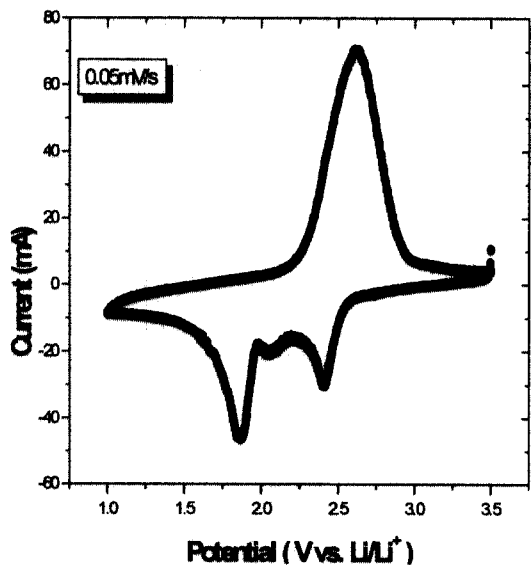

Fig. 6. The cyclic voltammetry of the Li/S cell.

the impedance spectra of the Li/S cell at 3, 2.1, 1.5 V of discharging potential respectively. From EIS analysis, the bulk resistance was similar with respect to discharging voltage changes but at 1.5 V, the charge transfer resistance was increased remarkably. It may be due to the formation of thick film on electrode surface. Fig. 8a) and 8b) shows the

SEM images of the sulfur electrode after the cell cycled 50th between 2.1 V and 3.5 V and the cell cycled 50th between 1.5 V and 2.5 V. From this figure, it can be seen that the cell cycled between 2.1 V and 3.5 V shows no film formed on electrode surface but the cell cycled between 1.5 V and 2.5 V shows film formed on electrode surface.

From these results, the degradation mechanism of Li/S cell was proposed like this. When the cell is discharged, sulfur reacts with Li ion and produces the lithium polysulfides that can be easily dissolved into electrolyte. Some lithium polysulfides can diffuse out from electrolyte. These lithium polysulfides react further with Li ion and produce the lithium
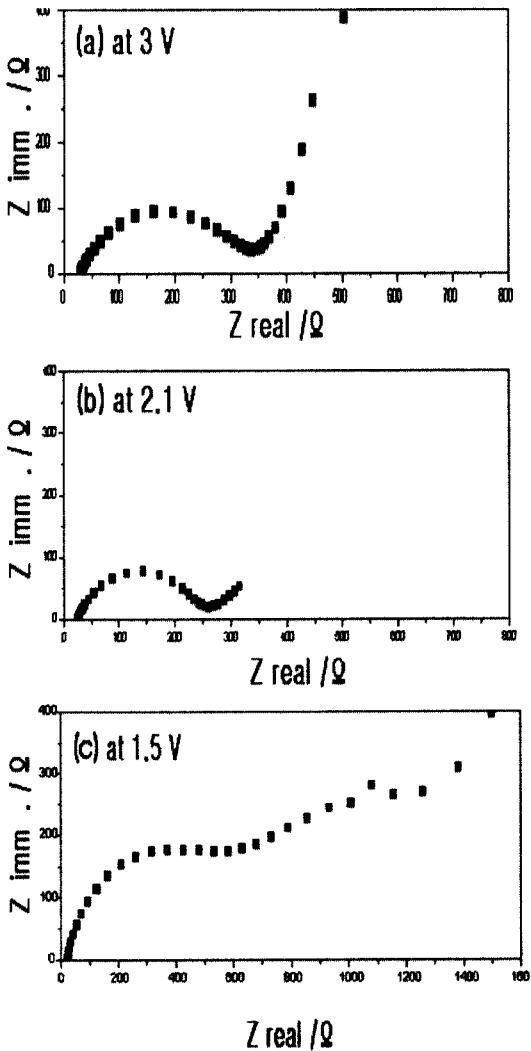

Fig. 7. The impedance spectra of the Li/S cell at 3V(a), 2.1V(b), 1.5V(c) of discharging potential respectively.
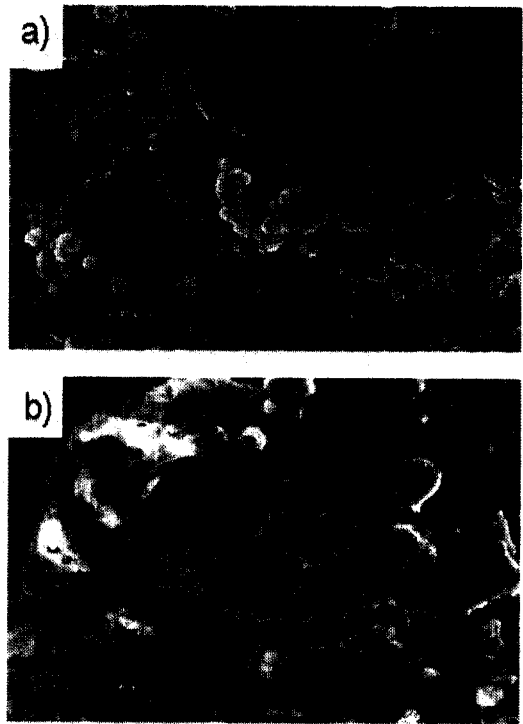

Fig. 8. The SEM images of the sulfur electrode after the cell cycled 50th between 2.1 V and 3.5 V(a) and the cell cycled 50th between 1.5 V and 2.5V(b).

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sulfide, Li_2S. But some lithium polysulfides produce the Li_2S on the electrode surface and then they disturb the Li ion movement and have poor contact with carbon matrix. So this film increases and becomes thicker with the cell cycling. This may be the main cause of the degradation of the Li/S cell. The lithium polysulfides would dissolve into electrolyte, but if they would not diffuse out to electrode surface, the cycle life of the Li/S cell will be improved.

4. Conclusion

The cycling behavior of the Li/S cell was studied with two cutoff potentials of 1.5 V to 2.5 V and 2.1 V to 3.5 V. The reaction of the lower voltage plateau of the Li/S cell was degraded faster than that of the upper voltage plateau of the Li/S cell. After 50th cycles, thick film formed on electrode surface was observed. The cause of the degradation of Li/S cell may be due to the thick Li_2S film formation on sulfur electrode surface.

Acknowledgement

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