ELSEVIER

Journal of Power Sources 109 (2002) 89–97

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Preparation and electrochemical properties of lithium–sulfur polymer batteries

Byoung Ho Jeon[a], Jin Hee Yeon[a], Kwang Man Kim[b], In Jae Chung[a,*]

[a]*Department of Chemical Engineering, Korea Advanced Institute of Science and Technology, (KAIST), 373-1 Kusong, Yusong, Taejon 305-701, South Korea*

[b]*Battery Technology Team, Telecommunication Basic Research Laboratory, Electronics and Telecommunications Research Institute (ETRI), 161 Kajong, Yusong, Taejon 305-350, South Korea*

Received 18 September 2001; received in revised form 17 January 2002; accepted 18 January 2002

Abstract

The lithium/sulfur (Li–S) batteries consist of a composite cathode, a polymer electrolyte, and a lithium anode. The composite cathode is made from elemental sulfur (or lithium sulfide), carbon black, PEO, $LiClO_4$, and acetonitrile. The polymer electrolyte is made of gel-type linear poly(ethylene oxide) (PEO) with tetra ethylene glycol dimethyl ether. Cells based on Li_2S or sulfur have open-circuit voltages of about 2.2 and 2.5 V, respectively. The former cell shows two reduction peaks and one oxidation peak. It is suggested that the first reduction peak is caused by the change from polysulfide to short lithium polysulfide, and the second reduction peak by the change from short lithium polysulfide to lithium sulfide (Li_2S, Li_2S_2). The cell based on sulfur has the same reduction mechanism as that of Li_2S, which is caused by the multi process (first and second reduction) of lithium polysulfide. On charge–discharge cycling, the first discharge has a higher capacity than subsequent discharges and the flat discharge voltage is about 2.0 V. As the current load is increased, the discharge capacity decreases. One reason for this fading capacity and low sulfur utilization is the aggregation of sulfur (or polysulfide) with cycling. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Sulfur; Lithium secondary battery; Lithium sulfide; Polymer electrolyte

1. Introduction

A battery based on the lithium/elemental sulfur redox couple has a theoretical specific capacity of 1600 mAh/g based on active material, and a theoretical specific energy of 2600 Wh/kg, assuming the complete reaction of lithium with sulfur to Li_2S. The use of sulfur is advantageous as it is a relatively cheap and non-poisonous material [1]. Therefore, the high capacity and low cost attract strong interest in developing Li–S batteries. The Li–S battery has a reduction–oxidation reaction mechanism which is different from that of commercial secondary lithium batteries (e.g. lithium-ion battery, lithium-ion polymer battery), in which the reaction mechanism of lithium metal oxide and graphite is based on an intercalation–deintercalation mechanism. In the secondary Li–S battery, lithium metal is oxidized and sulfur reacts with lithium ions during discharge [2–5]. The reverse occurs during charge

$$Li \rightarrow Li^+ + e^- \quad \text{(anode during discharge)}$$
$$S_8 + 16Li^+ + e^- \rightarrow 8Li_2S \quad \text{(cathode during discharge)}$$

Although the Li–S battery has many advantages, a Li–S battery with a sulfur cathode is impossible to the discharge fully at low temperature 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 [4,6].

It has been reported [7–11] that Li–S cells with liquid electrolytes have serious problems of low active-material utilization and poor cycle-life, due to the insulating nature of sulfur and Li_2S (final product of Li–S cell) and to the loss of active material in form of soluble polysulfide reaction products. Further problems are the incomplete reversibility of lower-order sulfides (e.g. Li_2S_2, Li_2S), and degradation and non-stability of the lithium electrode in liquid organic electrolytes.

Chu [4] showed that all solid Li–S cells have a high capacity value for a single discharge at a high temperature.

* Corresponding author. Tel.: +82-42-869-3916; fax: +82-42-869-3910.
E-mail address: chung@kaist.ac.kr (I.J. Chung).

0378-7753/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0378-7753(02)00050-2

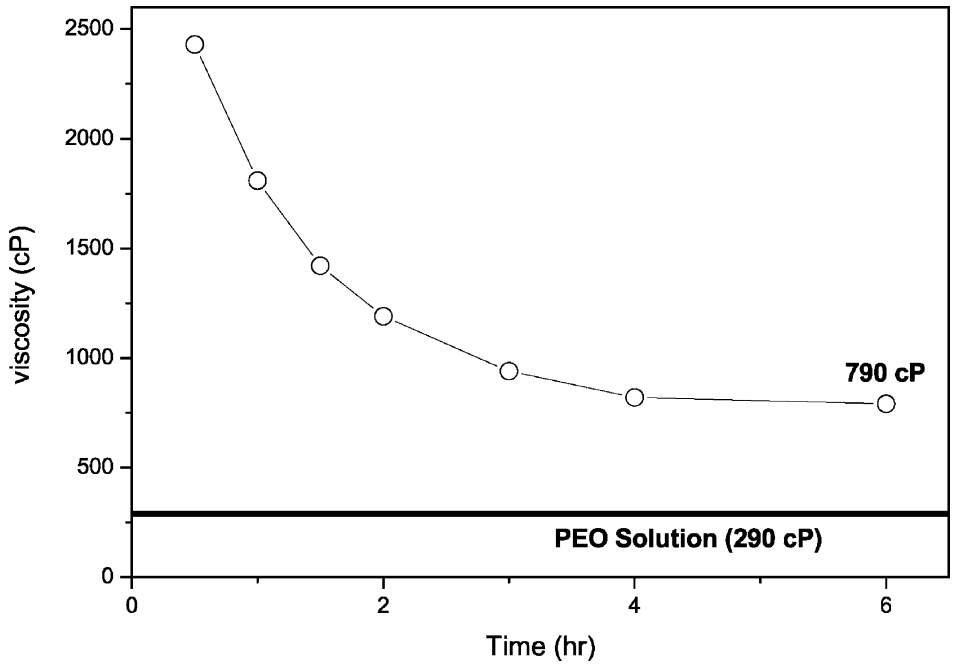

Fig. 1. Apparent viscosity of cathode slurry as a function of time in ball mill. Thick line is viscosity of PEO solution in acetonitrile.

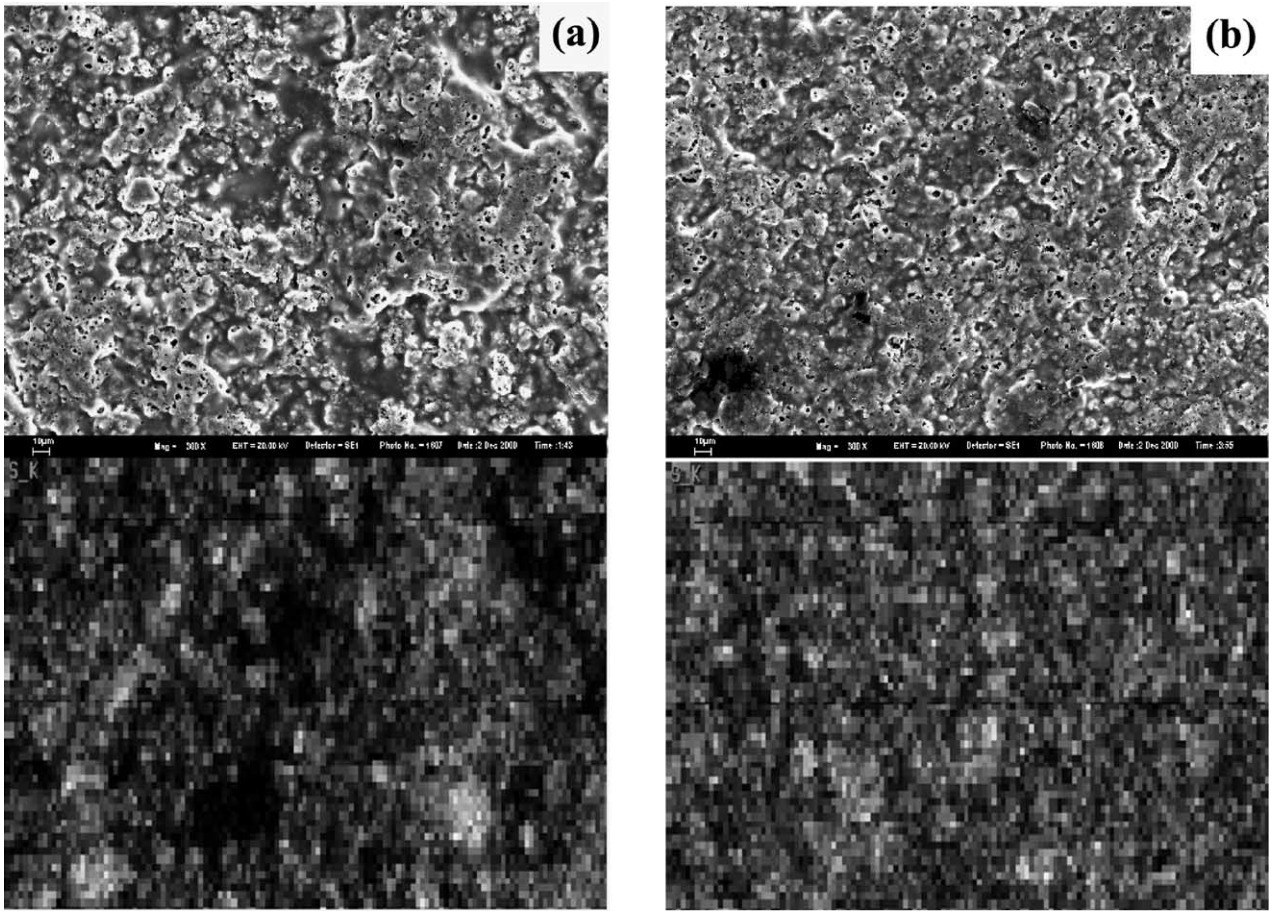

Fig. 2. SEM microscopy (upper picture) and EDS (lower picture, dot mapping of sulfur) of cathode film made by slurry at (a) 0.5 h (b) 1.5 h (c) 4 h and (d) 6 h.

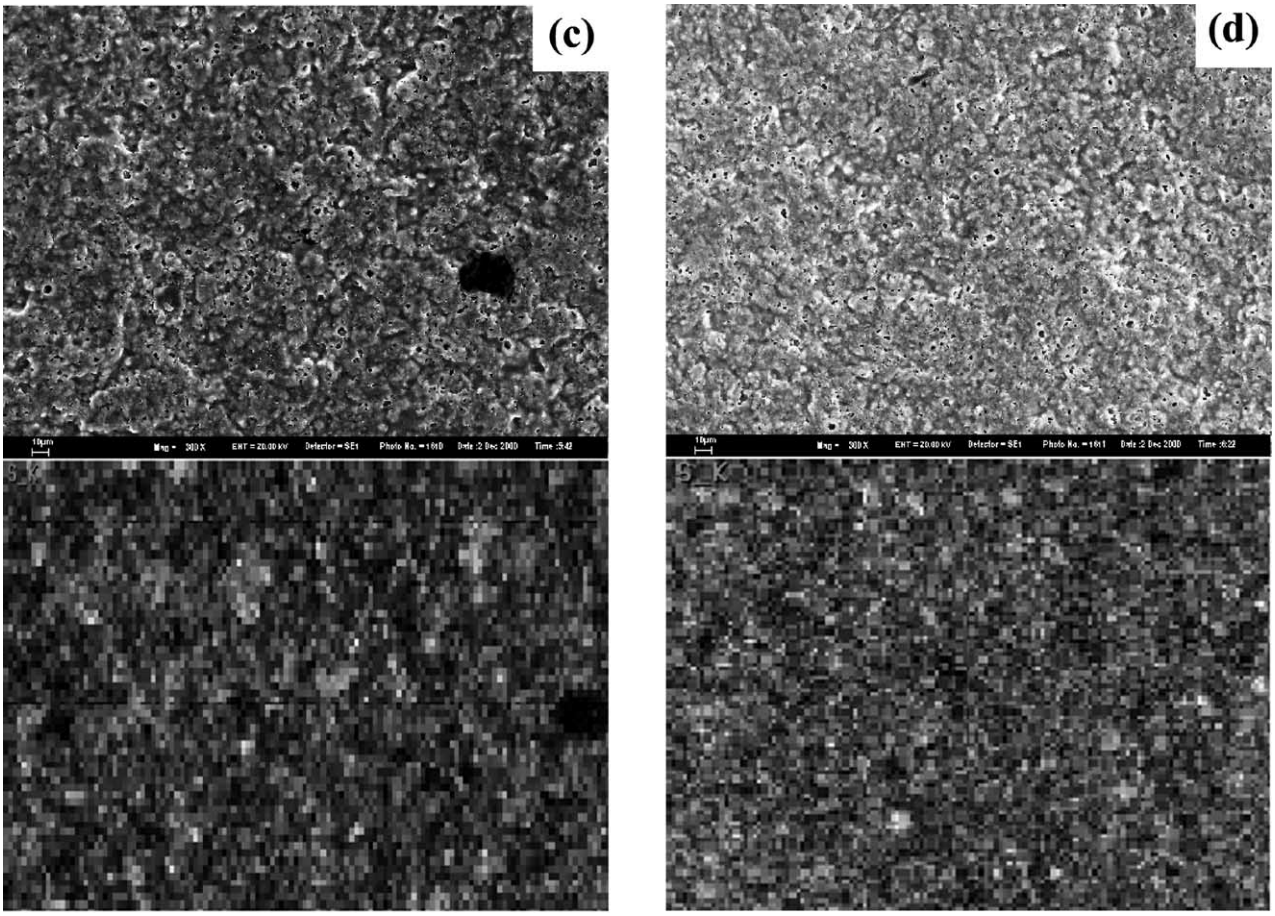

Fig. 2. (*Continued*).

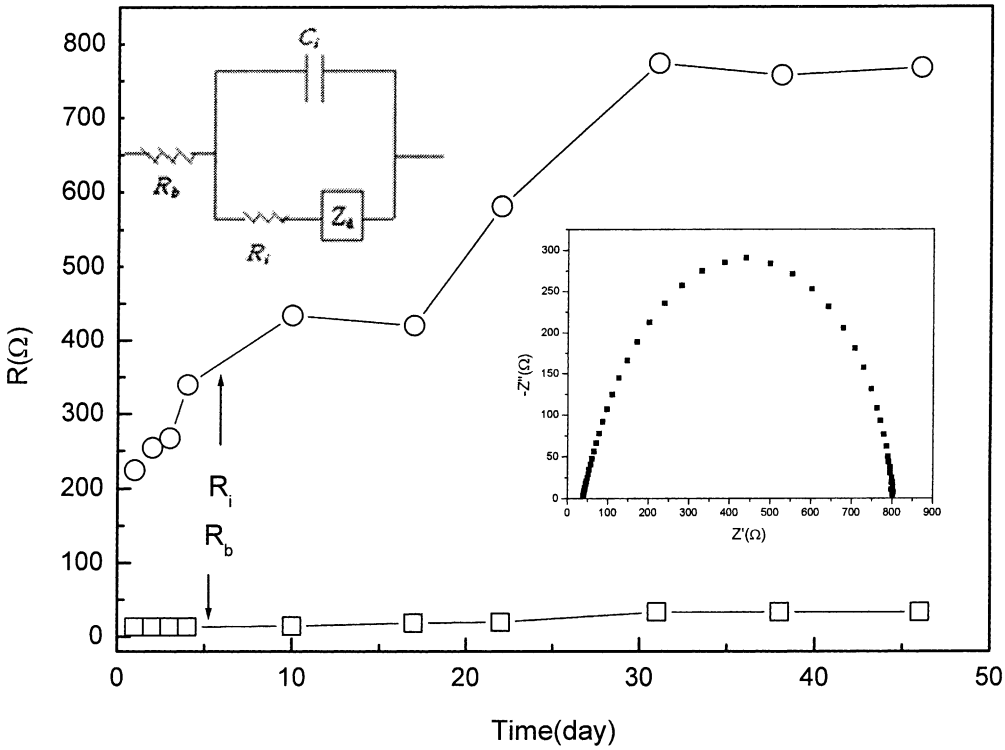

Fig. 3. The ac impedance spectrum of a Li/polymer electrolyte/Li cell and equivalent electrical circuit.

However, the decline of capacity with cycling, has been a persistent problem, and may be due to an irreversible loss of active cathode material. Peled and co-workers [8–11] suggested that some products of the polysulfide reduction became inactive or, at least, difficult to be oxidized. The products might be Li_2S and Li_2S_2.

Given the above, the first goal of this study is to prepare a composite cathode—a uniform mixture of active material (sulfur), conductive material (carbon black), and ionic conductor—and to investigate its electrochmical properties in a Li–S cell. Finally, an attempt is made to determine the reason for the reduction in capacity and the low sulfur utilization of the composite cathode when cycled in a Li–S battery.

2. Experimental section

2.1. Preparation of lithium/polymer electrolyte/sulfur (lithium sulfide) composite cathode

Sulfur (Aldrich, Sublimed sulphur) powder was prepared by ball-milling in a dry condition. A mixture containing 50 wt.% ball-milled sulfur (average particle size is 7.5 μm by centrifuge particle size analyzer), 15 wt.% carbon black (Super P black, dried before use at 140 °C under vacuum for 12 h), and 35 wt.% polyethylene oxide (PEO, Aldrich, $M_v = 5\,000\,000$) with $LiClO_4$, (ethylene-oxide unit:Li = 8:1) was ball-milled for 30 min. Acetonitrile (solvent:PEO ratio = 50:1 by weight) was poured

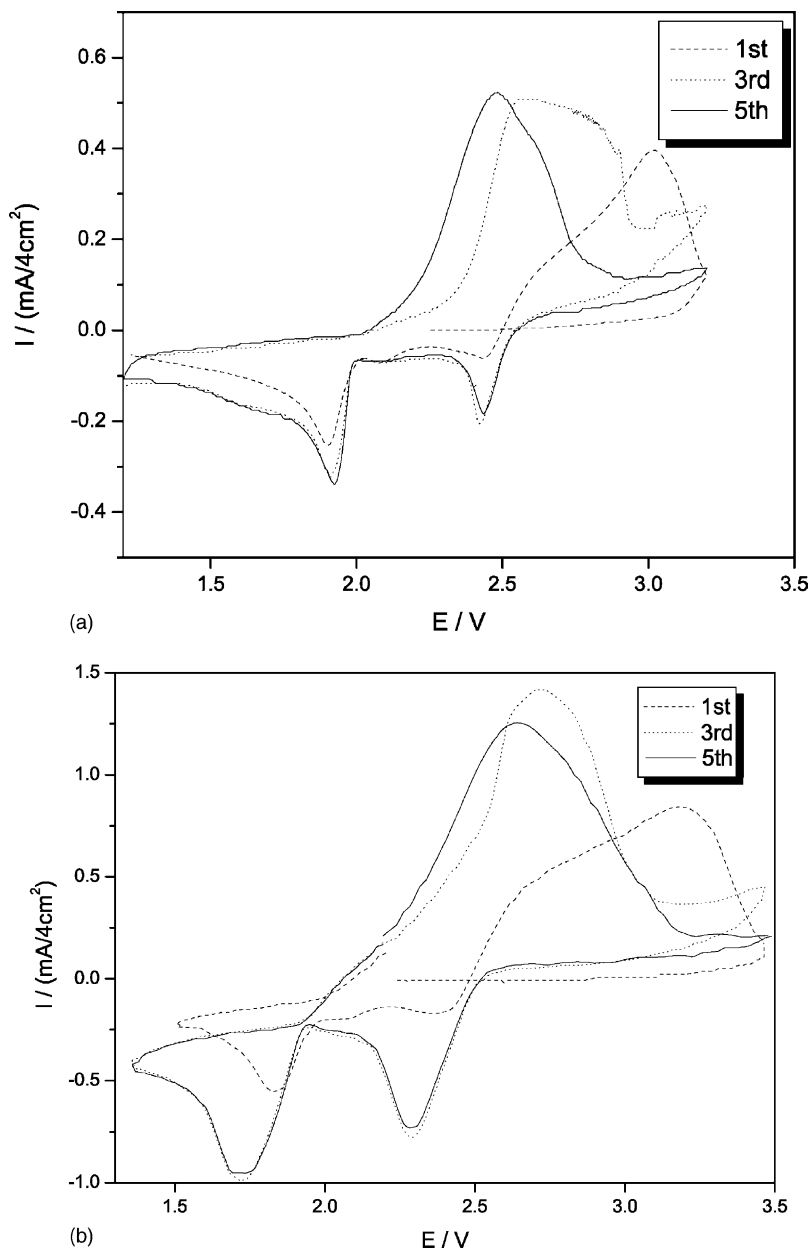

Fig. 4. Cyclic voltammograms for cell with Li_2S as active material of cathode. Sweep rate (a) 50 μV s^{-1}; (b) 100 μV s^{-1} at room temperature.

into this mixture and the slurry was ball-milled again to achieve uniform mixing. The slurry made of lithium sulfide (Li_2S, Aldrich) as active material was treated in a ball mill for 7 days at the same composition as the preparation of sulfur slurry. A thin cathode film was cast directly on to a stainless steel (SUS 304) current-collector, and the solvent (acetonitrile) was allowed to evaporate at ambient temperature. The final film was pressed with a twin roller, cut to dimensions of 2 cm × 2 cm and dried further under vacuum at 60 °C for 30 min. It was used as a cathode.

The lithium salt $LiClO_4$ (Aldrich) was dissolved completely in a solution of liquid tetraethylene glycol dimethylether (tetraglyme) (Grant Cor., battery grade) and acetonitrile (HPLC grade, N_2 purge for 1 day and molecular sieve treatment). Next, PEO (Aldrich, dried before use at 40 °C under vacuum for 12 h) was added to give a composition of EO:Li = 8:1 (EO: ethylene-oxide unit) at room temperature. The mixture was kept under continuous stirring until the PEO was dissolved completely. The resulting viscous solution was then poured into a Teflon vessel and the acetonitrile was evaporated. The film was used as a polymer electrolyte [13,14]. The entire preparation procedure was carried out in an environmentally controlled dry-box. The anode was prepared by pressing lithium foil on copper Exmet.

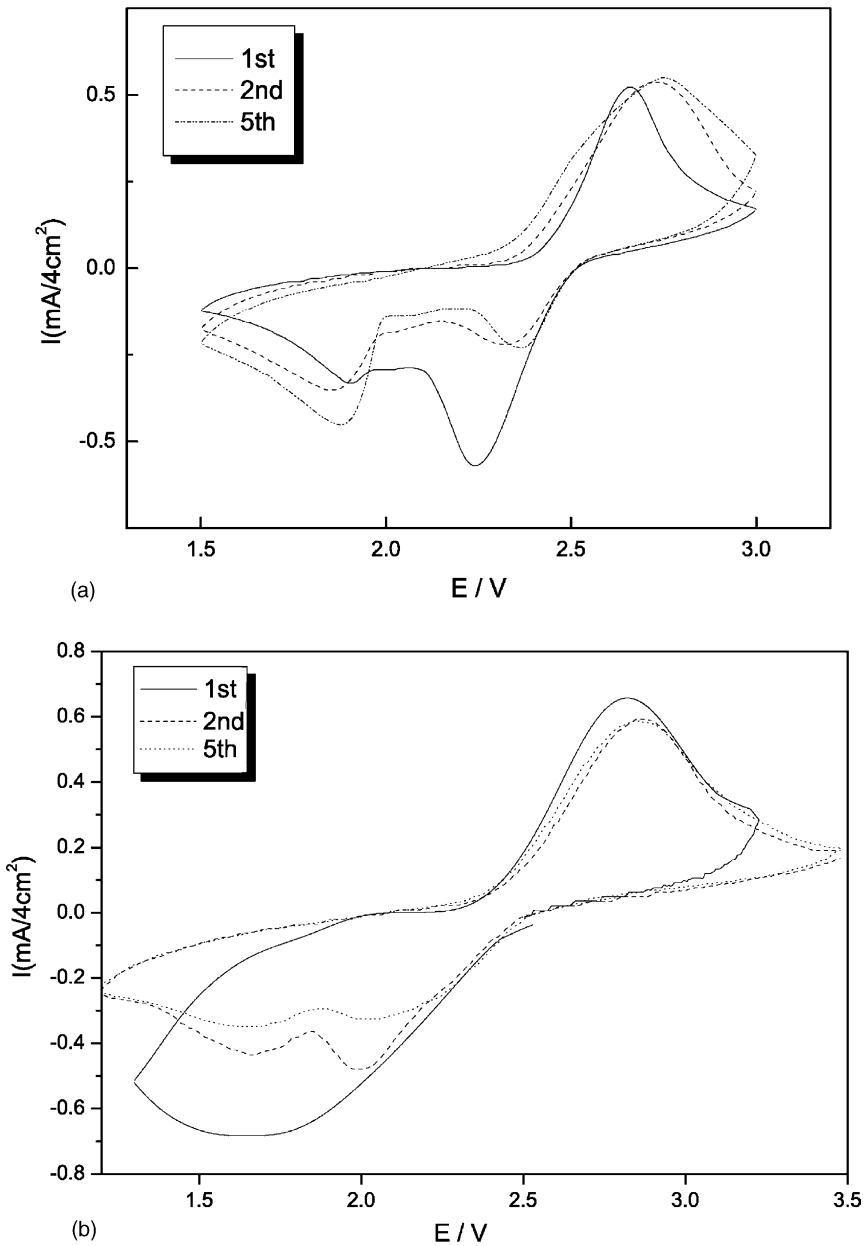

Fig. 5. Cyclic voltmmograms for cell with sulfur as active material of cathode. Sweep rate (a) 50 μV s^{-1}; (b) 200 μV s^{-1} at room temperature.

A cell composed of the anode, the electrolyte and the composite cathode was laminated and sealed in a bag under vacuum.

2.2. Measurements

Slurry viscosities were measured by means of a Brookfield viscometer at fixed time intervals in order to characterize the dispersion state. The morphology of the cathode film slurry was examined by scanning electron microscopy (LEO 1455VP) with energy dispersive spectroscopy (EDS) and a quadrant back-scattering detector (QBSD).

Cyclic voltammetry (CV) was used to characterize the redox behavior and the kinetic reversibility of the cell. Cyclic voltammograms were recorded by means of a Hokuto Denko HA-301 potentiostat/galvanostat with a *X–Y* recorder. A SUS 304 current-collector coated with the composite cathode was used as the working electrode. The counter and reference electrodes were lithium metal.

Battery performance was tested with a Maccor charger and a cut-off/galvanostatic cycling method was used.

3. Results and discussion

3.1. Preparation and characterization of battery components

The mixing sequence for the preparation of a cathode in a commercial lithium battery affects the viscosity and the battery performance because of differences in dispersion properties [12]. The preparation of a sulfur composite cathode with active material (sulfur), electrically conductive material, and ionic conductor is quite complex because of the insulation character of sulfur. The viscosity of a slurry made by attrition in a ball mill after premixing with sulfur, carbon black, and PEO for 30 min is shown in Fig. 1. The initial viscosity is above 2000 cP. The viscosity is stabilized after 4 h at about 800 cP, which is a higher viscosity than that for PEO solution in acetonitrile (290 cP). The stability of the slurry viscosity demonstrates that the components of the composite cathode are well-dispersed and uniform, as shown in Fig. 2. The upper image is a scanning electron micrograph and the lower picture is a EDS pattern (dot mapping method, white color is a sulfur trace). The results for a slurry after 0.5 h, (Fig. 2(a)) show many black regions, which are aggregates of sulfur. After 4 and 6 h, however, there are no black regions (Fig. 2(c) and (d)). This indicates that sulfur is well dispersed and the components of the composite cathode are uniform. Therefore, the cathode film is prepared from the slurry which is ball-milled for 6 h.

In this study, the ionic conductivity of the linear PEO polymer electrolyte determined by a frequency response analyzer, is 3.38×10^{-4} (S cm^{-1}) at room temperature. The ac impedance spectroscopy is used to investigate the interface between the lithium metal and the polymer electrolyte. For an assembled cell of Li/polymer electrolyte/Li, the impedance response was monitored for 46 days; the results are presented in Fig. 3. The equivalent electrical circuit is indicated in the left upper inset note, (Warburg diffusion impedance (Z_d) can be eliminated and this circuit is explanined in detail in [13–15].) The impedance response after 46 days is shown in the right inset. The bulk resistance (R_b) is unchanged and has a stable value. In contrast, the polymer electrolyte does not attain a stable interface with lithium until 30 days, as indicated by increase in charge

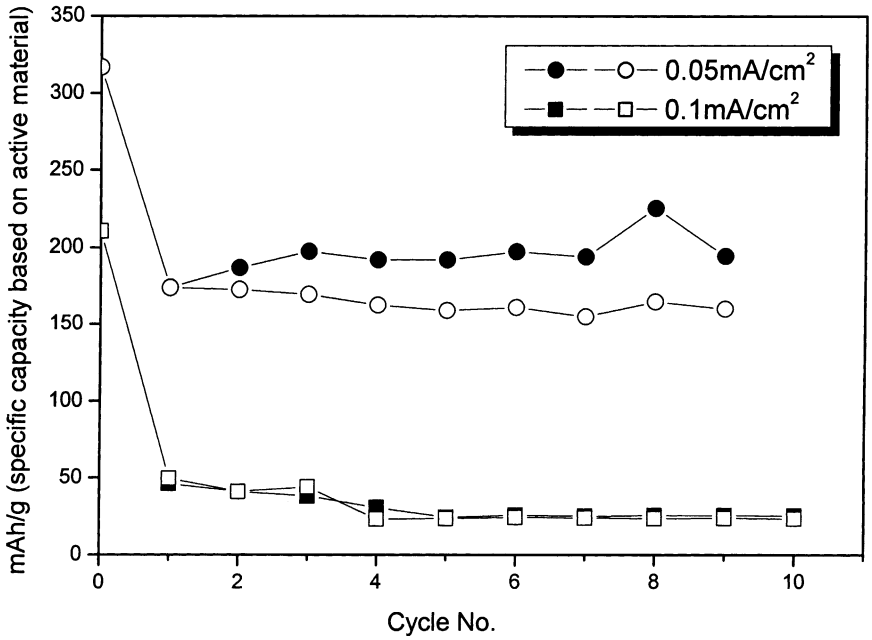

Fig. 6. Specific capacity based on active material (sulfur) as function of cycle number. Closed symbol is charge capacity, open symbol is discharge capacity.

transfer resistance (R_i). The passivating layer is stable after 30 days.

3.2. Electrochemical properties of cell made of lithium sulfide (Li_2S) as active material

In order to investigate the redox properties of the ultimate discharge product (Li_2S) of the Li–S battery, Li_2S was used instead of sulfur. Cyclic voltammograms for a cell made with Li_2S are expressed as a function of sweep rate in Fig. 4. The open-circuit voltage (OCV) of the cell is about 2.2 V. Since the cell is initially in the discharged state, the voltammogram is commenced by increasing the voltage. On the first scan, no oxidation peak is present up to 3 V at all sweep rates, but above 3 V, one oxidation peak appears. This peak corresponds to the oxidation of Li_2S to polysulfide. The next scan has an oxidation peak below 3 V. The oxidation at a low voltage indicates easy oxidation of Li_2S.

Two reduction peaks are also present in the voltammogram shown in Fig. 4. Polysulfide undergoes a multi-reduction: the first reduction peak is due to the change from polysulfide to short lithium polysulfide (Li_2S_n, $8 > n > 2$) and the second reduction peak takes place by the change from short lithium polysulfide to lithium sulfide (Li_2S, Li_2S_2). Similar results have been reported for the redox processes of lithium polysulfide in THF [16–18]. As the sweep rate increases, the peak potential of oxidation increases and that of reduction decreases, that is, the oxidation of Li_2S to polysulfide and the reduction of polysulfide of Li_2S become more difficult.

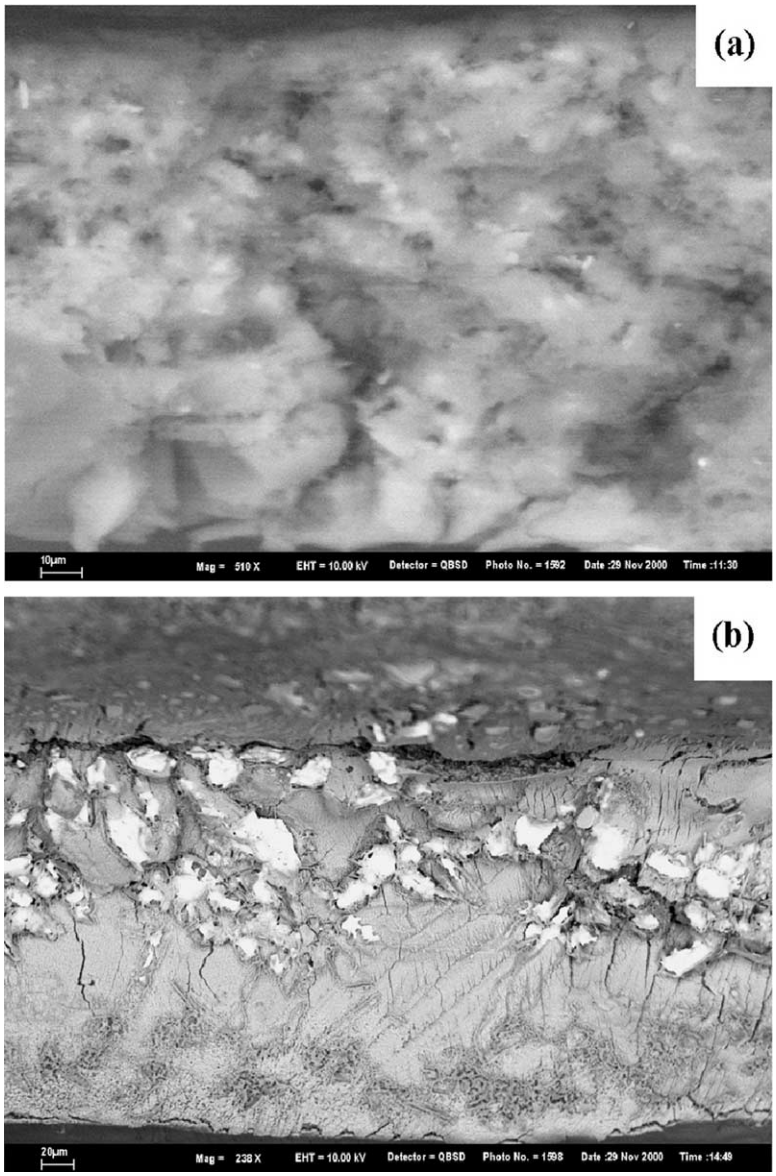

Fig. 7. QBSD morphology of SEM (a) before charge–discharge and (b) after 10th cycle.

3.3. Electrochemical properties and performance of Li–S battery

Cyclic voltammograms for a cell made with sulfur as the active material of the cathode are given in Fig. 5. Since the cell is charged in a state (OCV about 2.5 V), the voltammogram is commenced by scanning to lower voltages. The reduction of sulfur occurs in two stages as for Li_2S. At a sweep rate of 50 $\mu V\ s^{-1}$, the potential difference between the first and second reduction peaks is clearly distinguishable. At 200 $\mu V\ s^{-1}$ sweep rate, there are two peaks in the reduction but the difference between them is small. Two peaks indicate two ways of reduction: the first is for polysulfide to short lithium polysulfide and second is for short lithium polysulfide to lithium sulfide (Li_2S, Li_2S_2). As the sweep rate increases, the peak of oxidation shifts towards a higher voltage, and the oxidation to polysulfide becomes more difficult as in the cell made with Li_2S. It is noted form Fig. 5 that the cell has a larger capacity when the sweep rate is low.

The specific capacity of a Li–S cell based on sulfur as a function of cycle number is given in Fig. 6 (cut-off 1.7–2.7 V, constant current 0.05 mA cm^{-2} and 0.1 mA cm^{-2}). The first discharge has the higher the capacity. The flat discharge voltage is about 2.0 V. As the current load is increased, the discharge capacity is decreased. This result corresponds to difficult oxidation and reduction at a high sweep rate.

3.4. Morphology of composite cathode in Li–S battery

Morphologies obtained by QBSD before charge–discharge and after 10 cycles for a composite cathode and a polymer electrolyte are displayed in Fig. 7(a) and (b), respectively. The white areas in EDS analysis show the presence of sulfur. It is seen that sulfur is well dispersed

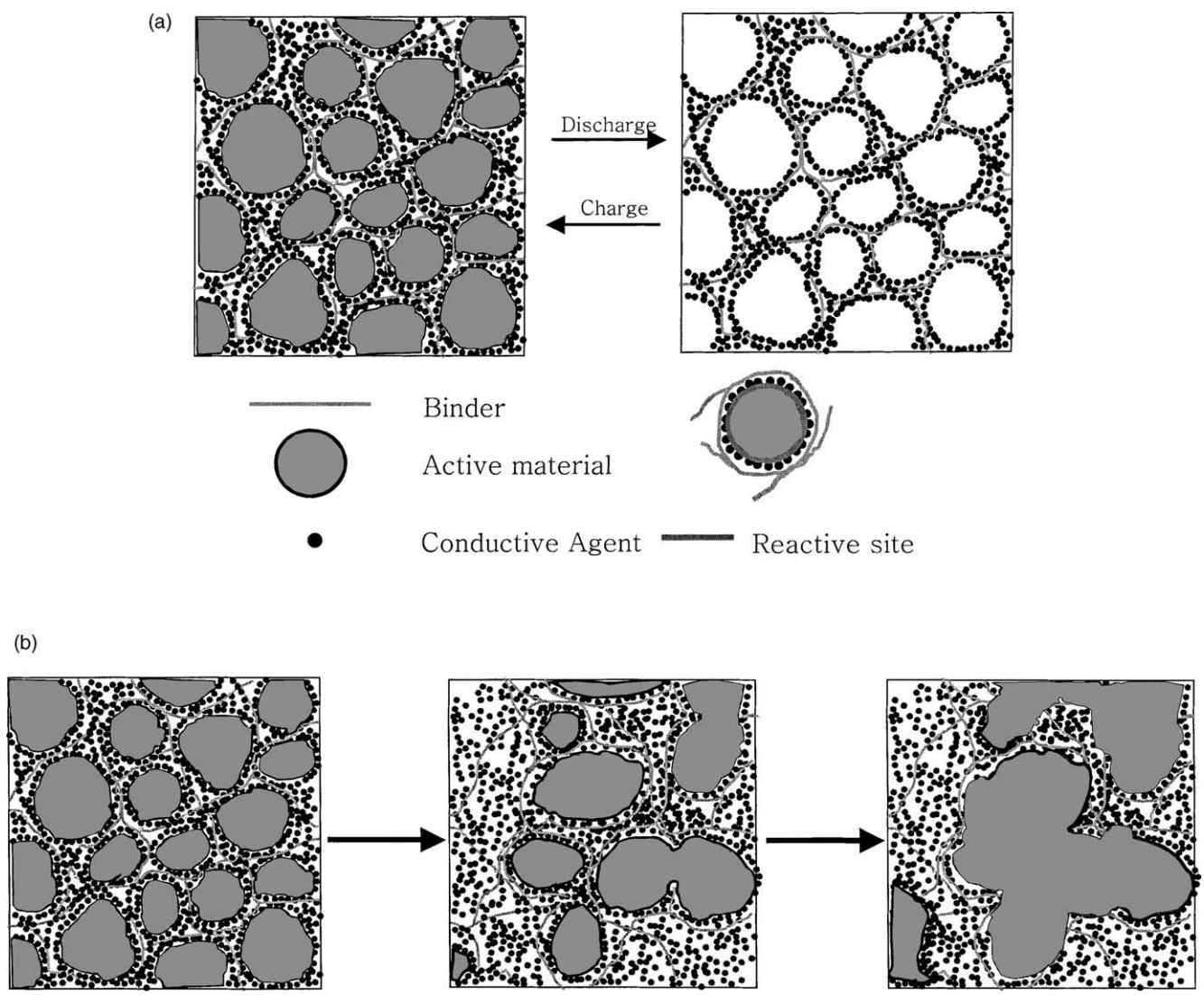

Fig. 8. Model for morphology change of composite cathode during charge–discharge: (a) ideal case; (b) real case.

in the composite cathode before the charge–discharge experiment but becomes aggregated after cycling.

A model for the change in morphology of the composite cathode during charge–discharge is given in Fig. 8. In an ideal case (Fig. 8(a)), sulfur retains its original space and the cathode continues to have a uniform distribution of components in the redox reaction (i.e. the charge–discharge process). In a real case (Fig. 8(b)), however, sulfur does not remain fixed in position and the distribution in the cathode is not uniform. Therefore, the cathode cannot have the well distributed morphology of the type shown in Fig. 7(a). This behavior is a major problem with composite cathodes in Li–S batteries, and cause poor cycle life and low sulfur utilization.

4. Conclusions

A composite cathode is prepared by attrition in a ball mill and has a well-dispersed morphology of sulfur. The open-circuit voltages of cells made of Li_2S or sulfur are about 2.2 and 2.5 V, respectively. Two reduction peaks and one oxidation peak are shown by each type of cell. The former two peaks indicate a multi-reduction process for lithium polysulfide. The first reduction peak is due to the change form polysulfide to short lithium polysulfide (Li_2S_n, $8 > n > 2$), and the second reduction peak takes place by the change from short lithium polysulfide to lithium sulfide (Li_2S, Li_2S_2). The flat discharge voltage is about 2.0 V. As the current load increases, the discharge capacity decreases. A composite cathode with sulfur cannot maintain well-distributed morphology and loses reactive sites between sulfur and lithium during charge–discharge cycling. Therefore, the Li–S cell has a poor cycle life and low utilization of sulfur.

Acknowledgements

The authors wish to express their gratitude for the advice and assistance of Dr. D.Y. Seung, Dr. C.H. Do, and S.I. Moon. This work has been carried out in a research programme of Samsung SDI and National Institute of Environmental Research (NIER).

References

[1] J.O. Besenhard, Handbook of Battery Materials, Wiley-VCH, 1998.
[2] R. Okuyama, E. Nomura, J. Power Sources 77 (1999) 164.
[3] J. Broadhead, T. Skotheim, J. Power Sources 65 (1997) 213.
[4] M.-Y. Chu, US Patent US05814420 (1998).
[5] T. Skotheim, US Patent US05601947 (1997).
[6] D. Marmorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, J. Power Sources 89 (2000) 219.
[7] R.D. Rauh, K.M. Abraham, G.F. Pearson, J.K. Surprenant, S.B. Brummer, J. Electrochem. Soc. 126 (1979) 523.
[8] H. Yamin, E. Peled, J. Power Sources 9 (1983) 281.
[9] H. Yamin, A. Gorenshtein, J. Penciner, Y. Sternberg, E. Peled, J. Electrochem. Soc. 135 (1988) 1045.
[10] E. Peled, T. Sternberg, A. Gorenshtein, Y. Lavi, J. Electrochem. Soc. 136 (1989) 1621.
[11] E. Peled, A. Gorenshtein, M. Segal, Y. Sternberg, J. Power Sources 26 (1989) 269.
[12] K.M. Kim, W.S. Jeon, I.J. Chung, S.H. Chang, J. Power Sources 83 (1999) 108.
[13] G.B. Appetecchi, G. Dautzenberg, B. Scrosati, J. Electrochem. Soc. 143 (1996) 6.
[14] K.M. Abraham, Z. Jiang, B. Carroll, Chem. Mater. 9 (1997) 1978.
[15] T.-C. Wen, W.-C. Chen, J. Power Sources 92 (2001) 139.
[16] H. Yamin, J. Penciner, A. Gorenshtain, M. Flam, E. Peled, J. Power Sources 14 (1985) 129.
[17] V. Merritt, T. Sawyer, Inorganic Chem. 9 (1970) 211.
[18] R.P. Martin, W.H. Dóub Jr., J.L. Roberts Jr., T.S. Donald, Inorganic Chem. 12 (1973) 1921.