

Electrochemical performance of lithium/sulfur batteries with protected Li anodes

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Abstract

The protection layer was introduced to the surface of the Li anode to enhance the charge/discharge performance of lithium/sulfur batteries. The protection layer was formed by a cross-linking reaction of the curable monomer in the presence of liquid electrolyte and a photoinitiator. When the Li anode is coated with the protection layer, the unit cells with a liquid electrolyte showed an enhanced charge/discharge performance as compared to cells based on a polymer electrolyte, resulting in an average discharge capacity of 270 mAh/g-cathode during 100 cycles. All the charge/discharge tests were performed at room temperatures.

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1. Introduction

Lithium ion batteries and lithium ion polymer batteries have been under intense research and development over the past 10 years due to their advantages such as high energy density, high operating voltage, low self-discharge rate, and no memory effect. However, there is still a need to enhance the capacity of the cathode in order to meet the performance needs of the new energy devices requiring high capacity. In fact, there is a limitation to the extent of lithium intercalation into transition metal oxides, which stimulates the research on lithium/sulfur rechargeable batteries.

Lithium/sulfur rechargeable batteries, which use sulfur as a cathode and Li as an anode, are very attractive for rechargeable lithium batteries due to their high theoretical specific capacity of 1675 mAh/g-active material, high theoretical energy density of 2600 Wh/kg, and low cost. The operating voltage of the lithium/sulfur battery, 2.1 V, is suitable for low-voltage electronic devices. In spite of these advantages of lithium/sulfur batteries, there are still many problems to be overcome for practical applications. Since sulfur is an insulating material, the electronically conducting phase and the lithium ion-conducting phase in the sulfur cathode must be

uniformly distributed. For lithium/sulfur batteries, lithium metal is used as the anode, i.e. as the lithium source to provide a high energy density. However, lithium is so reactive that it usually results in poor charge/discharge cycling efficiencies due to severe growth of the SEI layer [1–6]. For this reason, modification of the surface of the Li anode has been previously studied. For instance, Ogumi and co-workers [7,8] generated the protection layer on the Li anode by plasma polymerization, and Osaka et al. [9,10] induced the formation of a Li_2CO_3 layer on the surface of the Li anode by exposing the electrode to carbon dioxide. PolyPlus Co. [11] presented research on glass electrolytes sputtered on the Li anode and applied them to lithium/sulfur batteries.

In this work, the protection layer on the Li anode was newly prepared by a UV cured polymerization method. The protected Li anode was introduced to the lithium/sulfur battery to enhance the charge/discharge performance by reducing the growth of the SEI layer and suppressing the reaction between the Li and soluble polysulfides. The effect of the type of electrolyte on the charge/discharge performance was also investigated.

2. Experimental

2.1. Preparation of lithium and protected lithium anodes

The Li anode was prepared by laminating Li foil on a Cu current collector in a glove box. A curable, mixed solution

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consisting of the monomer (poly(ethylene glycol) dimethacrylate), liquid electrolyte (150–300 wt.% of the matrix polymer), and photoinitiator (methyl benzoylformate) was used to make the protection layer on the Li anode by the UV curing method. The thickness of the protection layer was about 10 μm .

2.2. Preparation of cathode

Sulfur (99.98%, Aldrich) and Super-P (MMM carbon) as a conducting agent were dried at 80 and 150 $^{\circ}\text{C}$ for 24 h under vacuum, respectively. A mixture of sulfur and Super-P was ball-milled, and then a P(VdF-co-HFP) solution in acetone was added to the mixture. After mixing the cathode

Table 1
Ionic conductivities at room temperature of plasticized polymer electrolytes^a as a function of EO:Li ratio

EO:Li ratio ^b	Mol. conc. (M)	Ionic conductivities (S/cm)
8:1	2.07	4.3×10^{-4}
16:1	1.09	6.5×10^{-4}
32:1	0.56	5.6×10^{-4}

^a P(VdF-co-HFP) containing TEGDME and LiClO₄.

^b The moles of the ethylene oxide repeating unit per mole of lithium ion in liquid electrolyte.

slurry for 2 days, it was cast on a glass plate and dried in air at room temperature. These cathodes were laminated with a mesh-type aluminum current collector at 150 $^{\circ}\text{C}$. The

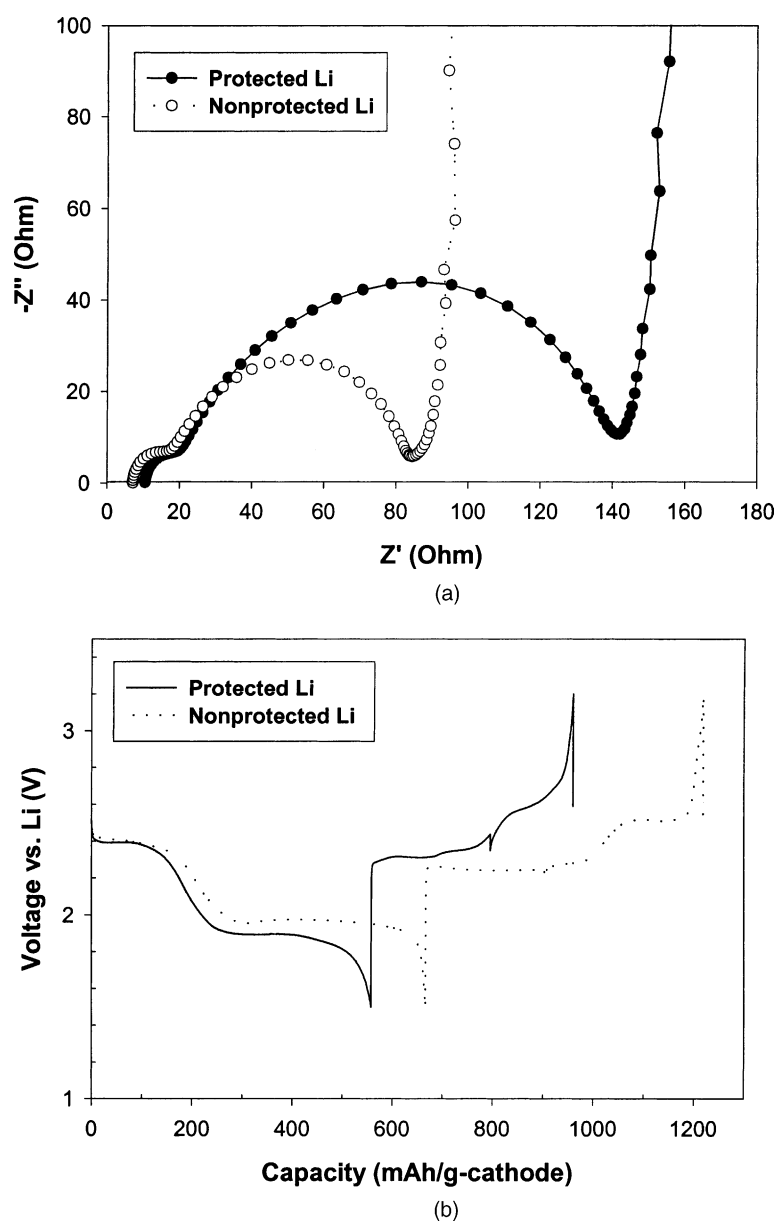


Fig. 1. (a) The initial ac impedance spectra of the Li/polymer electrolyte/S unit cells with protected and non-protected Li anodes; (b) the initial performance of the protected and non-protected unit cell.

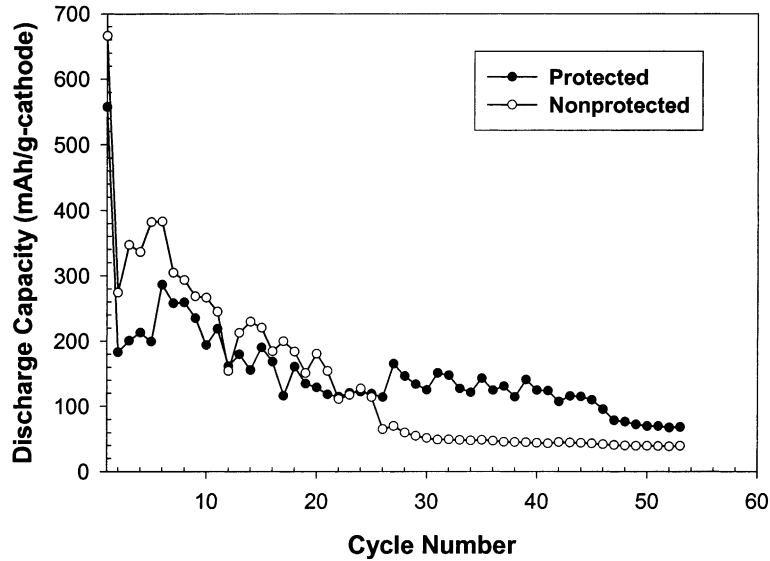


Fig. 2. The cycle life performance of the protected and non-protected unit cell at room temperature (C/10 charge/discharge rate).

prepared cathode has a composition of sulfur/Super-P/P(VdF-co-HFP) of 50/20/30 (wt.% ratio). The loading density of sulfur was about 2.0 mg/cm².

2.3. Preparation of polymer electrolyte

A copolymer of vinylidene fluoride and hexafluoropropylene (Kynar 2801, Atochem) was dried under vacuum

at 80 °C for 24 h. A plasticizer, tetra(ethylene glycol) dimethyl ether (TEGDME, Aldrich), and lithium perchlorate (99.99% LiClO₄, Aldrich) were used as received. After the PVdF copolymer was completely dissolved in acetone, the liquid electrolyte was added into the polymer solution and the mixed solution was further stirred. The amount of liquid electrolyte was 300 wt.% of the matrix polymer, which is enough to keep the mechanical strength

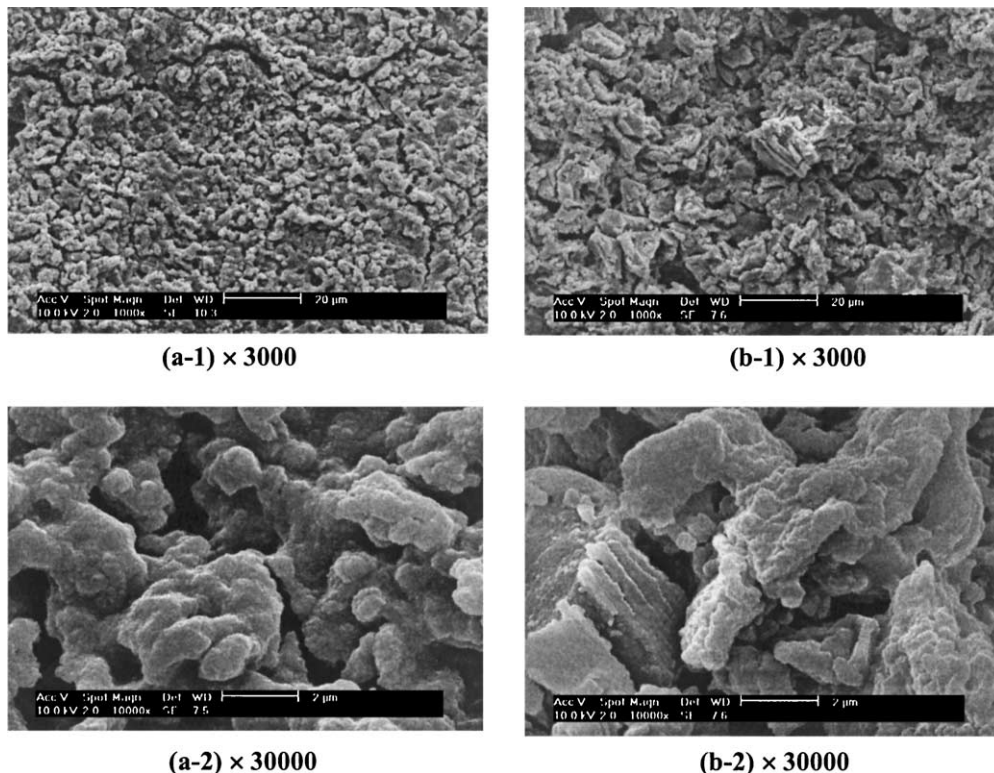


Fig. 3. The surface morphologies of the Li anode after 50 cycles: (a) the protected Li anode; (b) the non-protected Li anode.

of the polymer electrolyte. After complete homogenization of the mixture, the resulting viscous solution was cast on a substrate film with a doctor-blade and allowed to dry in a glove box at room temperature. The dried films were then removed from the substrate and used to assemble the cells. The thickness of the films was $140 \pm 10 \mu\text{m}$. All the preparations were conducted in a glove box purged with argon.

2.4. Preparation of unit cell

The manufactured cathode was immersed into the liquid electrolyte before cell assembly. The lithium/sulfur unit cell was made by stacking the plasticized polymer electrolyte

based on P(VdF-co-HFP) or separator containing liquid electrolyte between the sulfur cathode and the lithium anode. The cells were finally packaged in an aluminized polyethylene bag. The cell size was $2 \text{ cm} \times 2 \text{ cm}$.

2.5. Electrical properties measurements

Polymer electrolyte films or separators dipped in the liquid electrolyte were sandwiched between two stainless steel (SS) electrodes to measure the ionic conductivities. The ionic conductivities were obtained from the bulk resistance measured by ac complex impedance analysis using a Solartron 1255 frequency response analyzer (FRA) over a frequency range of 100 Hz to 1 MHz. The

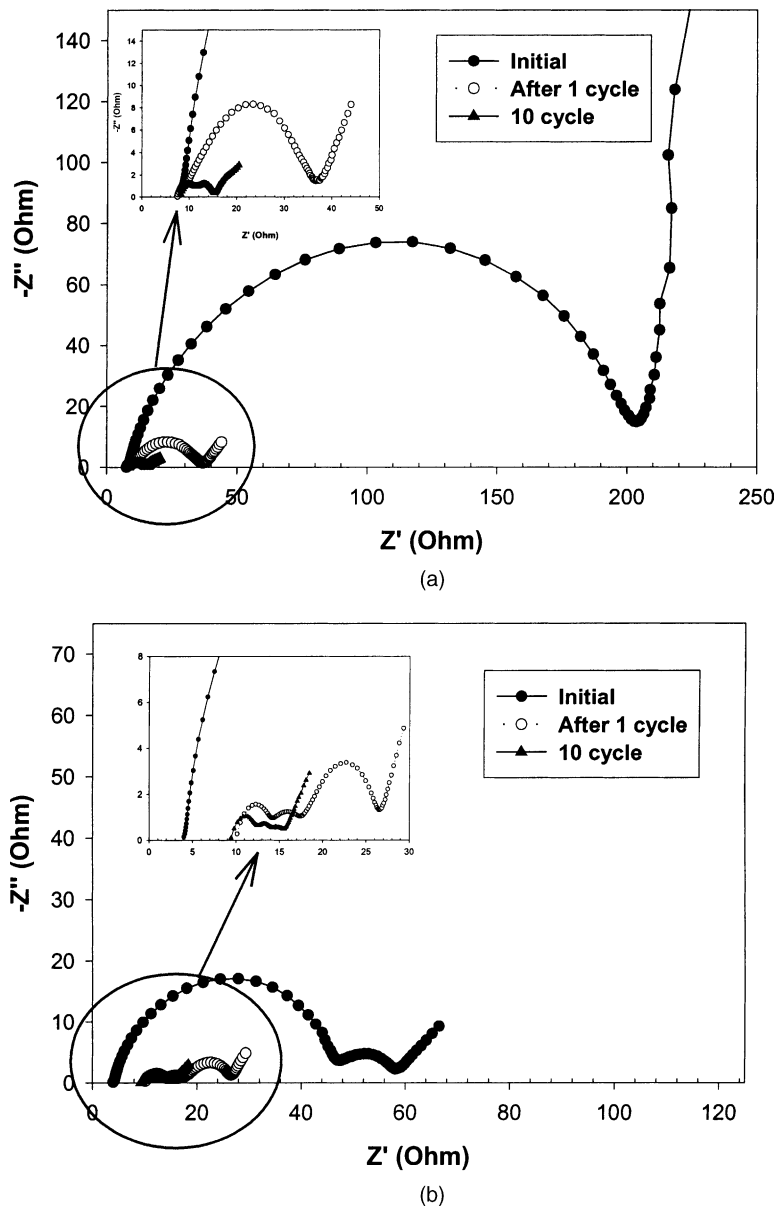


Fig. 4. The ac impedance spectra of (a) the protected Li/liquid electrolyte/S and (b) the non-protected Li/liquid electrolyte/S unit cells at room temperature after cycling.

impedance of the unit cell was also measured using a Solartron 1255 FRA to obtain the information at the interface between the polymer electrolytes or separators and the electrodes.

The unit cell was typically cycled between 1.5 and 3.2 V at a constant current density at room temperature using a TOSCAT-3000U (Toyo System Co. Ltd.).

2.6. Scanning electron microscopy (SEM)

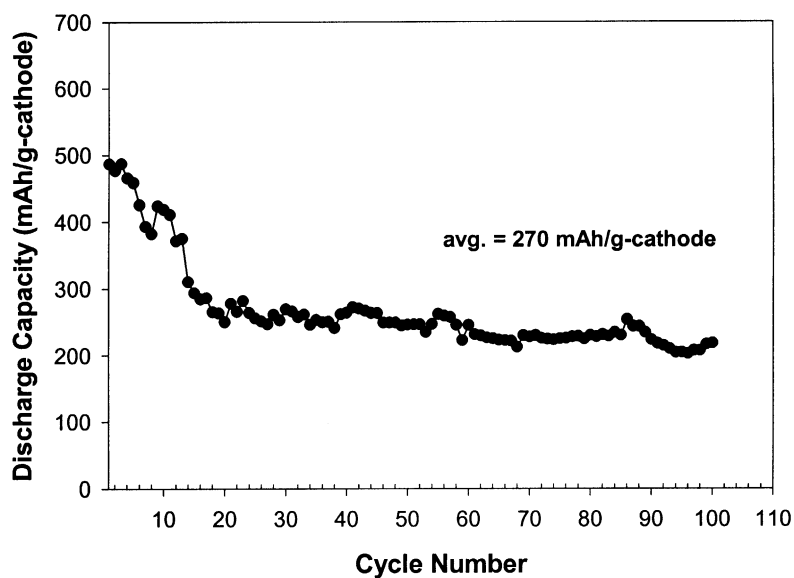
The morphology of the electrodes and electrolyte films were investigated by SEM using a Philips SEM 535M.

3. Results and discussion

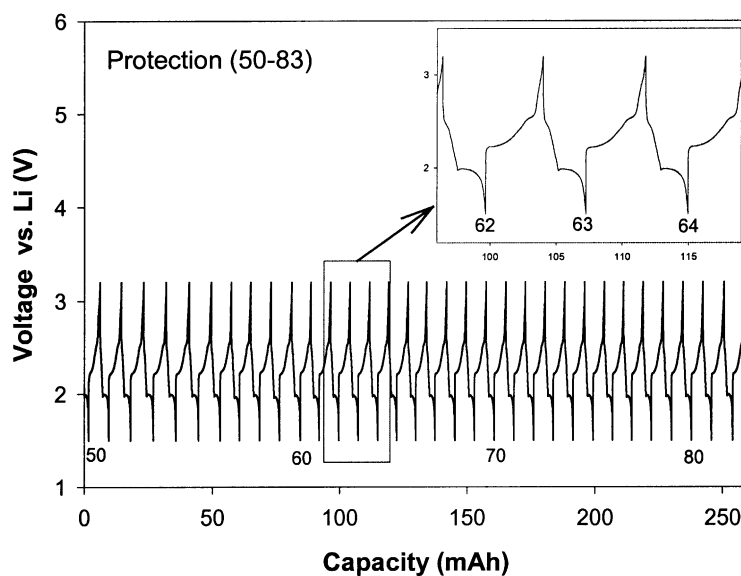
3.1. Unit cells with a plasticized polymer electrolyte

3.1.1. Ionic conductivity

The ionic conductivities of the plasticized polymer electrolytes based on P(VdF-co-HFP) as a function of salt concentration are listed in Table 1. The EO:Li ratio refers to the moles of the ethylene oxide repeating unit per mole of lithium ion in the liquid electrolyte. The maximum ionic conductivity at room temperature, 6.5×10^{-4} S/cm, was achieved when the EO:Li ratio is 16:1. So, the plasticized polymer electrolyte with an



(a)



(b)

Fig. 5. (a) Discharge capacities of the protected Li/liquid electrolyte/S unit cell as a function of cycle number; (b) charge/discharge profiles at a constant current density and 20 °C with 1.5 V cut-off.

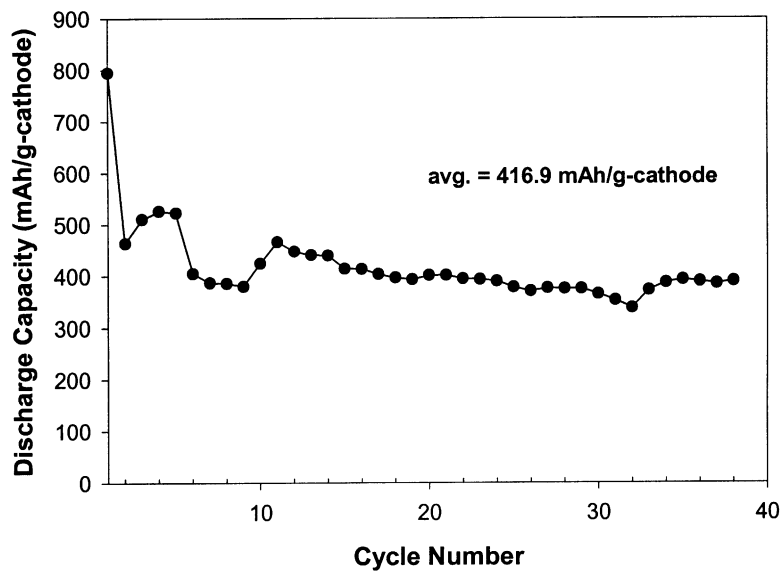
EO:Li ratio of 16:1 was used to assemble the unit cells.

3.1.2. Charge/discharge characteristics of unit cells

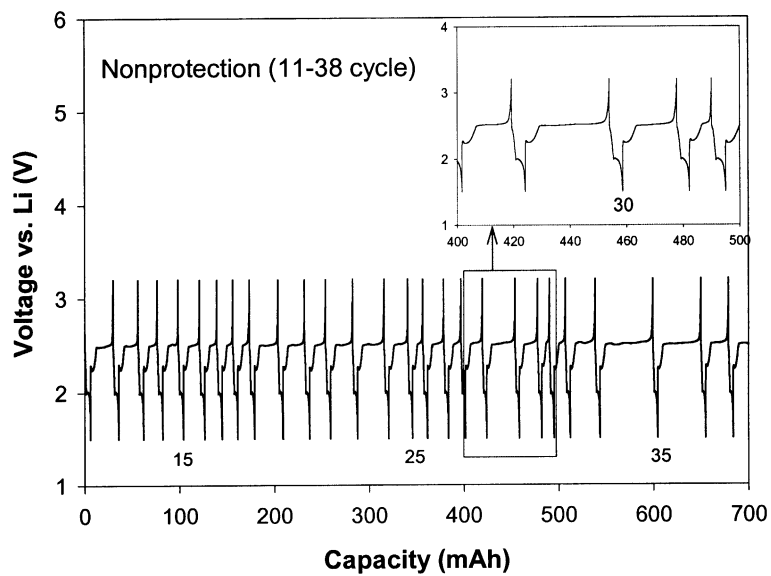
Fig. 1a shows the initial ac impedance spectra of the Li (protected or non-protected Li)/polymer electrolyte/sulfur unit cells at room temperature. The unit cell with the protected Li electrode showed a higher bulk and interfacial resistance than the cell without the protection layer. The presence of the additional protection layer caused an increase in the initial internal resistance of the unit cell, resulting in the lower capacity at the initial stage as shown in Fig. 1b. However, it is found from Fig. 2 that, after the first 25 cycles, the

discharge capacity of the unit cell, based on the protected lithium anode, starts to exceed the capacity of the cell without the protection layer. It indicates that the charge and discharge performance of the unit cell is more significantly dependent on the formation and growth of the SEI layer with cycling. The discharge capacity of the cell based on the protected Li anode after 50 cycles is found to be 150 mAh/g-cathode.

Fig. 3 comparatively shows the surface morphology of the Li anode with and without the protection layer after 50 cycles. The protection layer was peeled off carefully before the SEM images were acquired. The protected Li anode showed a smoother and denser surface morphology than the non-protected one.



(a)



(b)

Fig. 6. (a) Discharge capacities of the non-protected Li/liquid electrolyte/S unit cell as a function of cycle number; (b) charge/discharge profiles at a constant current density and 20 °C with 1.5 V cut-off.

3.2. Unit cell with a liquid electrolyte

In general, lithium/sulfur batteries with liquid electrolytes have been faced with the serious problem of low active material utilization and poor rechargeability due to the insulating nature of sulfur and Li_2S and to the loss of active

material in the form of soluble polysulfide products. Degradation of the Li electrode in liquid organic electrolytes is also a problem to be overcome in lithium/sulfur batteries. In connection with this, the lithium/sulfur battery system based on the liquid electrolyte using a membrane separator and the protected Li anode is considered in this work.

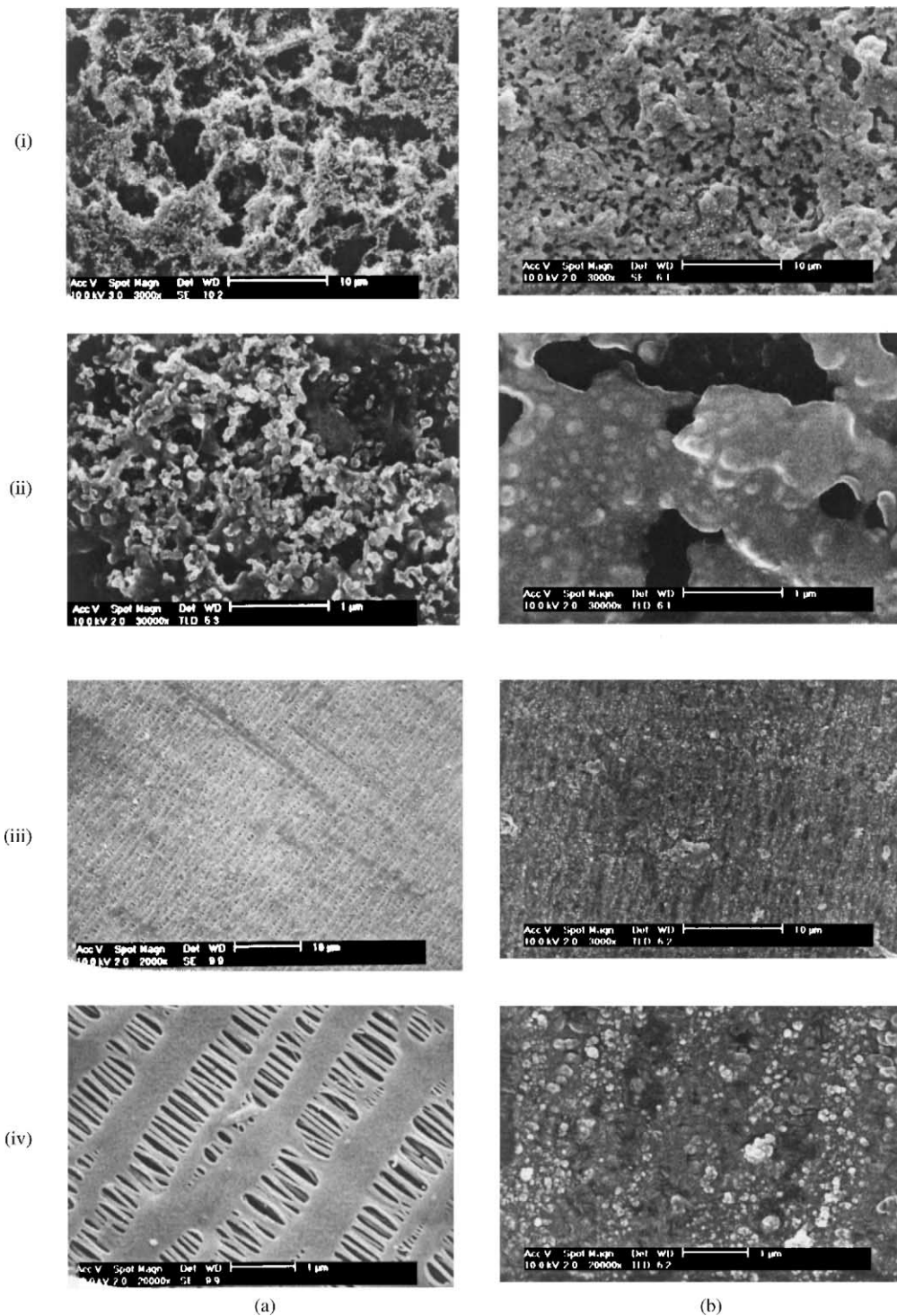


Fig. 7. The surface morphology ((a) before overcharging and (b) overcharged) of cathodes ((i) 3000 \times and (ii) 30,000 \times) and separators ((iii) 3000 \times and (iv) 30,000 \times).

3.2.1. Ionic conductivity

The ionic conductivity of the polypropylene separator (Celgard 2500, thickness = 25 μm , porosity = 47%) was measured after soaking in the liquid electrolyte. The liquid electrolyte is a mixture of TEGDME and LiClO_4 with an EO:Li ratio of 16:1. The ionic conductivity of the separator soaked with the liquid electrolyte was 1.9×10^{-4} S/cm at room temperature which is found to be much lower than that (6.7×10^{-4} S/cm) of the plasticized polymer electrolyte with the same EO:Li ratio. This seems to be due to a lower liquid electrolyte uptake for the separator containing liquid electrolyte.

3.2.2. Charge/discharge characteristics of unit cells

The lithium/sulfur unit cells, which are composed of a sulfur cathode (sulfur/carbon/P(VdF-co-HFP) = 50/20/30), a separator soaked in liquid electrolyte, and a protected Li anode, were prepared and cycled at room temperature.

Fig. 4a presents the ac impedance spectra of the protected Li anode/liquid electrolyte/S unit cell at room temperature with cycles. It is interestingly found that the interfacial resistance of the unit cell based on the protected Li anode/liquid electrolyte/S decreased sharply as the number of cycles increased resulting in about 1/30 of the initial interfacial resistance at the 10th cycle. This may be associated with the formation of a stable SEI layer between the Li anode and protection layer and an increase in the content of the liquid electrolyte in the protection layer during cycling.

Fig. 5a shows very stable discharge capacities of the unit cell based on the protected Li anode/liquid electrolyte/S after around 20 cycles. The charge/discharge profiles in Fig. 5b are also shown to be very stable and reproducible. The average discharge capacity is found to be 270 mAh/g-cathode within 100 cycles which is twice as high as the discharge capacity of the cathode used in conventional lithium ion batteries.

For the case of a Li anode with a protection layer, it is found that the discharge capacity of the cell based on the liquid electrolyte is much higher than that based on the polymer electrolyte. It may be caused by a lower bulk resistance due to a thinner thickness (25 μm) of the separator compared to the polymer electrolyte ($\approx 120 \mu\text{m}$) and an easier charge transfer reaction in the cathode due to the low viscosity of the liquid electrolyte.

Fig. 6a shows the cycle life performance of the non-protected Li/liquid electrolyte/S unit cell. The discharge capacity of this unit cell is a little higher than that of the protected Li/liquid electrolyte/S unit cell in early cycles. It can be explained by the fact that the unit cell with the non-protected Li anode showed lower interfacial resistance in Fig. 4b due to the absence of the additional resistance layer. However, it is shown from Fig. 6b, representing the charge/discharge profiles, that for the unit cell based on the non-protected Li/liquid electrolyte/S system there is a significant overcharge taking place around 2.5 V during the charge

Table 2

The appearance of overcharge phenomena for the unit cell systems

	Plasticized polymer electrolyte	Separator
Protected Li	No	No
Non-protected Li	No	Overcharge

process. This phenomenon is related to the reaction of polysulfide with Li at the anode. It is also observed that the overcharge becomes more significant with cycling. It means that the required time to charge the unit cell becomes longer with cycling, so we could not check the cycle performance over 40 cycles.

The increase in the interfacial resistance due to the presence of a protection layer does not seem to influence the cell performance so significantly as the retardation of polysulfides. Because the difference in the interfacial resistance between the protected and non-protected lithium electrode-based cells is shown to become less significant with cycles in Fig. 4.

The morphology of the overcharged cells is shown in Fig. 7. The carbon black in the cathodes seem to be surrounded with lithium sulfides which are produced by the reductive reaction of sulfur in the cathode. The pores of the separators are clogged with polysulfides or other reaction products.

3.3. Effect of Li protection

By comparing the charge/discharge profiles of the cells with or without the protection layer, the role of protection layer can be estimated. The only case where overcharge phenomena takes place is shown in Table 2. The overcharge did not take place for the unit cell with the protection layer or the plasticized polymer electrolyte. In other words, the polymer components have the effect of preventing the overcharge phenomenon. It is thought that the dense polymer structure can reduce the migration of polysulfides from the cathode to the Li anode. Therefore, the introduction of polymer components in the electrolyte or on the surface of the Li anode is desirable in lithium/sulfur batteries to prevent overcharge.

It is thus suggested that the cell with a protected Li anode/liquid electrolyte/S cathode is a good candidate for high performance lithium/sulfur batteries.

4. Conclusions

A protected Li anode was introduced to lithium/sulfur batteries to enhance the cycle performance. The unit cells based on the protected Li anode and liquid electrolyte showed a very stable discharge capacity up to 100 cycles, which seemed to be due to the formation of a stable SEI layer. The average discharge capacity of the unit cell was 270 mAh/g-cathode. The protection layer on the Li anode could also suppress the overcharge during the charge process.

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