Suppression of polysulfide dissolution by polypyrrole modification of sulfur-based cathodes in lithium secondary batteries

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Abstract

In order to solve the problem of polysulfide dissolution into the electrolyte on sulfur-based cathodes, we propose a novel method of modifying the S cathode by coating it with a polypyrrole (PPy) film, which is prepared by oxidative electropolymerization using a solution consisting of, 1-methyl-1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and pyrrole. The PPy film demonstrates a high Li^+ transport number. The film

also exhibits a superior ability to inhibit polysulfide dissolution into the electrolyte during the charge-discharge cycles. Furthermore, the charge-discharge properties of the coated cathode is evaluated using an electrolyte consisting of 1.0 M LiTFSI in a mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL), which is known to easily dissolve polysulfides. Because of the surface modification with the PPy film, the cathode exhibits excellent specific capacities of 823 and 354 mAh g⁻¹ at C-rates of 0.1 and 1.0 C, respectively, with high coulombic efficiency. Thus, the strategy of coating the S cathode with PPy is successful in inhibiting the polysulfides dissolution even in electrolytes known to easily dissolve polysulfides, besides allowing high C-rate operation. Further, the modification of the S cathode allows the selection of a suitable electrolyte based on the anode, rather than being limited by the cathode.

Keywords: Sulfur-based cathode, Polypyrrole, Electropolymerizing, Li-ion permselectivity, Polysulfide dissolution

1. Introduction

Li/S batteries are one of the candidates suitable for the next-generation high energy density batteries. However, the S cathode has several existing problems that

need to be solved. Some of the issues associated with the S cathodes include low ionic/electronic conductivity of S and Li_2S , large volume expansion of S (~80% expansion) upon lithiation, and the dissolution of the intermediate products, namely lithium polysulfides (Li_2S_x , where $4 \leq x \leq 8$), into the electrolyte [1,2]. Various strategies have been developed to solve these problems. While there has been extensive discussions regarding the solutions for improving the ionic/electronic conductivity of the cathodes and the volume expansion of S upon lithiation [3,4], the inhibition of polysulfide dissolution into the electrolyte persists as the most important challenge. Carbon nanotubes with fine pores have been successful in suppressing the dissolution of polysulfides into the electrolyte [5]. While, the use of glyme-based electrolytes has been successful in suppressing the polysulfide dissolution [6,7]. However, batteries containing electrolytes involving ionic liquids such as glyme show a relatively high resistance owing to the high viscosity of the electrolytes. Therefore, batteries containing an electrolyte with an ionic liquid have a limit on the charge-discharge capabilities at high C-rates. On the other hand, there have been many reports on methods for suppressing the dissolution of polysulfides by coating or modifying the surface of an active material with a polymer using chemical oxidative polymerization [8,9]. In these experiments, it is important to adjust the homogeneity of the electrode and strict

controls are needed to produce optimal nanostructures.

In this communication, the S/Ketjenblack (S/KB) cathode, which is one of the typical S-based cathodes in use, was coated with an electropolymerized polypyrrole (PPy) film. A p-type conductive polymer is suitable for coating the sulfur cathode because the polymer has to be polymerized at a higher potential than the reaction potential of sulfur. PPy was selected because side reactions hardly occur and polymerization from a non-aqueous solvent is easy. It is easy to obtain film-like polymers that strongly adsorb on the electrode surface using electropolymerization [10]. In addition, a pinhole-less PPy film can be obtained by electropolymerization [11]. Thus, the PPy film is expected to suppress the dissolution of polysulfides, while allowing the permeation of Li^+ into the organic solution. Therefore, a PPy-coated cathode is likely to have desirable properties as a modified S cathode. After proper modification of the S/KB cathode with the PPy film, the charge-discharge properties of the PPy-S/KB cathode were characterized in an electrolyte containing 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in a mixed solvent consisting of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 vol.%), at various C-rates. The choice of the electrolyte is particularly advantageous at high C-rates, owing to its low viscosity.

2. Experimental

2.1. Material synthesis

The S/KB composite cathode was evaluated for use as a S-based cathode. The S/KB composite was prepared by mixing S powder (Aldrich) with Ketjenblack in a 1:1 weight ratio using a granulator (Balance Gran, Akira Kiko). The mixture was then heated in an Ar atmosphere at a temperature of 155 °C for 12 h to form a composite of S and KB. The S/KB composite slurry was prepared in the granulator by mixing 90 wt.% of the S/KB composite and 10 wt.% of polyvinylidene difluoride (PVdF) binder (Aldrich) with N-methylpyrrolidone (NMP), which acted as the solvent. In order to prepare the S/KB composite cathode, the slurry was applied to a Ni substrate using the doctor blade method and dried for 24 h in a dry atmosphere (at the dew point of below -40 °C, RT).

The PPy-coated S/KB (PPy-S/KB) cathode was prepared using oxidative electropolymerization by constant-potential control in a three-electrode cell. The S/KB cathode, which was 1 cm × 1 cm in size, was used as the working electrode, while a Pt wire and a Li foil were used as the counter electrode and the reference electrode, respectively. The polymerization bath was composed of an ionic liquid solution

containing 1-methyl-1-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI, Toyo Gosei), 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Kishida Chemical Co., Ltd.), and 0.1 M pyrrole (Wako Pure Chemical Industries). The PPy was coated on the S/KB composite cathode at a constant anodic potential of 4.5 V. The amount of charge passed was 1.0 C cm^{-2} and the bath temperature was 80 °C.

2.2. Material characterization

The microstructure of the S/KB composite cathodes with the PPy modification were observed using field-emission scanning electron microscopy (FE-SEM, S4500S, HITACHI). The permselectivity of Li^+ through the PPy film was evaluated by using the principle proposed by E. Bakker et al. [12]. Briefly, the ion selective electrode was immersed in the sample solution with a suitable reference electrode and analyzed by measuring the potential shift between the electrodes. The electrode response potential (electromotive force; emf) was measured in the electrochemical cell system (Lithium titanium oxide (LTO) electrode, 1.0 M LiTFSI BMP-TFSI (std.) / Vycor glass / sample solution // PPy film // 1.0 M LiTFSI BMP-TFSI, LTO electrode).

In order to prepare the working electrode, which is separated by the PPy film,

the PPy film was polymerized directly onto a Ni substrate using the conditions described previously and peeled off from the substrate. Subsequently, the working electrode was prepared by adhering the PPy film (6 mm in diameter) to the end of a glass tube containing an LTO electrode and filled with an internal solution containing a 1.0 M LiTFSI BMP-TFSI standard solution. The internal solution for the outer reference electrode consisted of 1.0 M LiTFSI BMP-TFSI, which was the same as that for the working electrode. Various concentrations of LiTFSI in the sample solutions, namely 1.0 M, 1×10^{-1} M, 1×10^{-2} M, and 1×10^{-3} M, were studied, with BMP-TFSI as the solvent. As potential shifts, the open-circuit voltages (OCV) were measured at 80 °C, at intervals of 1 h, in order to obtain the stable potential shift. UV-Vis measurements (V-630, JASCO Co.) were carried out for evaluating polysulfide dissolution. For the UV-Vis measurements, the separators were removed from the disassembled coin cells after the charge-discharge cycles, and the separators, which is containing the electrolyte, were immersed in 5.0 mL of fresh electrolyte solutions. The extracted electrolyte solutions were analyzed in a quartz cell using UV-Vis spectroscopy.

2.3. Electrochemical battery performance measurements

Coin type 2032 cells were assembled in an Ar filled glove box, with 1.0 M

LiTFSI DME/DOL (1:1 vol.%) as the electrolyte, 25 μm thick polypropylene as the separator, Li metal foil as the anode, and PPy-S/KB as the cathode. The average S loading in the cathode was 0.5 mg cm^{-2} . For the charge-discharge tests, the cut-off potential and the charge-discharge rate were 1.5-3.0 V vs. Li and 0.03 C ($25\text{ }\mu\text{A cm}^{-2}$), respectively. The specific capacity is calculated by the mass of sulfur which ratio in the PPy-S/KB cathode is 38 wt.%. The charge-discharge characteristics were determined at room temperature.

3. Results and discussion

Fig. 1 (a) and (b) show the top view and the cross sectional FE-SEM images of the PPy film, respectively. Small particles of S and KB were not observed in the images, thereby confirming a uniform coating of the PPy film on the surface of the S/KB cathode. The cross section of the sample was prepared by cutting the sample with precision scissors and the SEM image of the cross section did not show any peel-off between the PPy film and the S/KB composite cathode. This clearly indicates that the PPy film is in good contact with the S/KB cathode surface. The thickness of the PPy film was determined to be about 1.2-1.5 μm , as shown in Fig. 1 (b). The condition and thickness of an electropolymerized film would be dependent on the supporting

electrolyte of the polymerization solution [11]. In this experimental condition, the PPy film thickness does not grow indefinitely, which mean the PPy film is pinhole-less. If there is a pinhole on the film, polymerization reaction does not stop.

Insert Figure 1

The PPy film was formed at a relatively high potential of 4.5 V at 80 °C, to stabilize a relatively large anion doped in the PPy film [13]. Generally, a redox reaction of PPy proceeds via the doping-undoping reaction of the anion (TFSI⁻, in this case) [14]. However, it is known that when a large polyanion is doped in the PPy film, some cation exchange characteristics manifest themselves in films [15]; on the other hand, when Li⁺ with a large diffusion coefficient is present in the film, the characteristics also appear that are doped with even low-molecule-weight dopant anions (ClO₄⁻, TOS⁻, TFSI⁻) [16, 17]. Since the polymerization bath contains TFSI⁻, the TFSI⁻ is doped in the PPy film. Thus, for a film formed under such conditions, high permeability of Li⁺ would be expected. In order to confirm the permselectivity of the electropolymerized PPy film toward Li⁺ ions, the PPy film was evaluated using the technique reported by E. Bakker, et al. [12]. Fig. 2(a) shows the shift in the potential of PPy film from the potential with the sample solution of 1.0 M LiTFSI, against Li⁺ concentration of the sample solution. The magnitude of the potential shift of the PPy electrode decreased with a decrease in

the Li^+ concentration in the solution. The theoretical slope calculated by the Nernst equation with the Nernst constant at 80 °C of 70 mV is also plotted in the figure. Since the measured data accorded with the theoretical slope, the Li^+ transport number of the PPy film was close to unity. Therefore, the Li^+ ion migrated to the Li^+ poor side from the Li^+ rich side, whereas the anion (TFSI^-) was left behind in the Li^+ rich side, producing the film potential shift. The above results show that the PPy film is permselective toward the Li^+ ions.

In order to examine the ability of the PPy film for the inhibition of polysulfide dissolution, the electrolyte solution was analyzed using UV-Vis spectroscopy, after the charge-discharge cycles were conducted. Coin cells were assembled using the S/KB composite cathode with and without modification by the PPy film, in order to conduct the charge-discharge tests. In the case of the S/KB composite cathode, the charge current continued to flow at ca. 2.5 V, even after the capacity reached the theoretical value during the 2nd cycle and further cycles could not be continued (Fig. S1). This overcharge mechanism is known as the shuttle phenomenon, where polysulfide is dissolved in the electrolyte between the electrodes [2]. On the other hand, in the case of the PPy-S/KB composite cathode, the shuttle phenomenon was not observed. Therefore, the PPy-S/KB cathode after the 10th cycle was used for the UV-Vis analysis, in order to

study the most severe conditions in this test. The UV-Vis spectra for the electrolyte from the cells cycled with PPy-S/KB and S/KB composite cathodes are shown in Fig. 2(b). The spectra shown in the figure were obtained by subtracting the blank data. In the case of the S/KB composite cathode, a significant absorption peak was observed in the wavelength range of 250-320 nm, which is attributed to elemental S and long-chain polysulfides [18]. The presence of this peak indicates that a considerable amount of elemental S and polysulfides are dissolved into the electrolyte. On the other hand, in the case of the PPy-S/KB cathode, the peak in the same wavelength range was very weak, indicating that the polysulfide dissolution was suppressed by coating PPy on the S/KB cathode, even in the 1.0 M LiTFSI DME/DOL (1:1, vol.%) electrolyte, which is known to easily dissolve the polysulfides. Therefore, it should be concluded that the prepared PPy film demonstrated selective transmitting properties for the Li^+ ions, whereas it did not allow the permeation of the polysulfide anion.

Insert Figure 2

Finally, Figs. 3(a) and (b) show the charge-discharge profiles and the C-rate performances of coin cell (Li // 1.0 M LiTFSI DME/DOL // PPy-S/KB). During the experiments, the C-rates were changed from 0.1 C to 1.0 C, and then reverted to 0.1 C. From Fig. 3(a), a voltage plateau that is characteristic of S, was observed in the

charge-discharge curves. With an increase in the C-rate, the voltage corresponding to the plateau shifted to a higher value during the charge cycle, whereas it shifted to a lower value during the discharge cycle. Furthermore, the plateau near 2.8 V, which represents the occurrence of the shuttle phenomenon, was not observed in the case of the PPy-S/KB composite cathode. The coulombic efficiency was observed to be over 95% during all the cycles and after 40 cycles, it reached a value of over 98%. This would be owing to the high Li^+ permeability and the inhibition of polysulfide dissolution, in the case of the PPy film modified S/KB cathode. At C-rates of 0.1 C, 0.2 C, 0.4 C, 0.8 C, and 1.0 C, the specific capacities were 823 mA h g^{-1} , 669 mA h g^{-1} , 546 mA h g^{-1} , 403 mA h g^{-1} , and 354 mA h g^{-1} respectively, at the end of 10 cycles for each C-rate. The capacity was recovered to 697 mA h g^{-1} when the C-rate returned to 0.1C from 1 C after 120 cycles. Thus, it was demonstrated that the PPy-S/KB cathode can deliver a high capacity of 354 mA h g^{-1} , even at a high C-rate of 1.0 C (0.84 mA cm^{-2}).

Insert Figure 3

4. Conclusions

In this study, we proposed a novel S cathode structure consisting of a film formed on a S-based electrode surface, where the film acted as a suppressant for polysulfide permeation. The PPy film, which was prepared by oxidative electropolymerization at a

relatively high polymerization potential to trap large anions, demonstrates ion-selectivity toward Li^+ only, with the transport ratio of nearly unity in the organic solution. The PPy film-coated S-based cathode was confirmed to have a superior ability for inhibiting polysulfide dissolution. In addition, even in a 1.0 M LiTFSI DME/DOL electrolyte, which is known to dissolve polysulfides easily, the PPy-S/KB cathode exhibited capacities of 823 mA h g^{-1} and 354 mA h g^{-1} at 0.1 C and 1.0 C, respectively. The simple structure prepared by directly coating the PPy film on the cathode, enabled the suppression of polysulfide dissolution into the electrolyte, thereby inhibiting the shuttle phenomenon. Thus, coating PPy on the S-based cathode is an extremely attractive method, since this allows the flexibility of choosing electrolytes according to the choice of the anode. Furthermore, the suppression of polysulfide dissolution thanks to the permselectivity of Li^+ makes the PPy-S/KB electrode an attractive cathode material for use in Li/S batteries.

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Fig. 1. FE-SEM images of the PPy-S/KB composite cathode: (a) top surface view ($\times 0.6$ k) and (b) cross-sectional view ($\times 3.0$ k).

Fig. 2. (a) Shift in the potential of the working electrode, which is separated by the PPy film, from the value obtained with 1.0 M LiTFSI solution against the different Li-ion concentration solutions of 1×10^x M LiTFSI in BMP-TFSI ($0 \leq x \leq -3$) and (b) UV–Vis

absorption spectra of the extracted solution prepared from the electrolyte obtained from the cells containing a S/KB composite cathode (after two cycles) and a PPy-S/KB composite cathode (after 10 cycles). The spectra were subtracted the blank data obtained with a fresh electrolyte solution from the spectra for the sample solutions.

Fig. 3. (a) Typical charge–discharge voltage profiles of Li // 1.0 M LiTFSI DME/DOL // PPy-S/KB coin cell cycled at various C-rates and (b) performance of a Li // 1.0 M LiTFSI DME/DOL // PPy-S/KB coin cell 0.1 C to 1.0 C.

Figure 1.

Figure 2.

Figure 3a.

Figure 3b.