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Graphical Abstract

Bifunctional separator as a polysulfide mediator for highly stable Li-S batteries

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ABSTRACT

The shuttling process involving lithium polysulfides is one of the major factors responsible for the degradation in capacity of lithium–sulfur batteries (LSBs). Herein, we demonstrate a novel and simple strategy—using a bifunctional separator, prepared by spraying poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) on pristine separator—to obtain long-cycle LSBs. The negatively charged SO_3^- groups present in PSS act as an electrostatic shield for soluble lithium polysulfides through mutual coulombic repulsion, whereas PEDOT provides chemical interactions with insoluble polysulfides (Li_2S , Li_2S_2). The dual shielding effect can provide an efficient protection from the shuttling phenomenon by confining lithium polysulfides to the cathode side of the battery. Moreover, coating with PEDOT:PSS transforms the surface of the separator from hydrophobic to hydrophilic, thereby improving the electrochemical performance. We observed an ultralow decay of 0.0364% per cycle when we ran the battery for 1000 cycles at 0.25 C—far superior to that of the pristine separator and one of the lowest recorded values reported at a low current density. We examined the versatility of our separator by preparing a flexible battery that functioned well under various stress conditions; it displayed flawless performance. Accordingly, this economical and simple strategy appears to be an ideal platform for commercialization of LSBs.

Keywords

Lithium–sulfur batteries; PEDOT:PSS; Separators; Graphene; Expanded graphene

Introduction

The human use of energy has grown steadily in response to increased population, economic growth, and advancements in technology. Inevitably, there is higher demand for next-generation high-capacity energy storage materials [1-11]. For example, much research has been conducted in the field of high-energy batteries. Sulfur—a naturally abundant and inexpensive side product of many industrial processes—is an ideal material for use in high-energy storage systems. Accordingly, lithium–sulfur batteries (LSBs) have attracted great interest in recent years because their theoretical capacity and theoretical energy density (1675 mA h g^{-1} and 2500 W h kg^{-1} , respectively) are much higher to those of lithium ion batteries (LIBs)[12-23]. Therefore, LSBs are attractive systems that might become future replacements for typical LIBs.

The application of LSBs has been plagued, however, by many drawbacks, including rapid decays in capacity, the insulating nature of active sulfur ($5 \times 10^{-30} \text{ S cm}^{-1}$ at 25°C), and shuttling phenomena, resulting from the high solubility of lithium polysulfides (Li_2S_x , $4 \leq x < 8$) in organic electrolytes, during electrochemical charge/discharge processes[9, 12, 13, 24-26]. Recently, considerable efforts have been exerted to overcome the reversible capacity and cycling stability to realize practical LSBs, including studies of sulfur-based composites [16, 20, 27-36], modification of lithium anodes [37-40], and the use of organic electrolytes and binders [26, 37, 41-46]. While each of these methods can play an important role in improving the electrochemical performance of LSBs, the required material processing steps can be elaborate, involve rigorous chemical synthesis, and use very low loadings of sulfur active mass, thereby limiting the chances of commercialization of viable LSBs.

A separator, an indispensable component of the battery, is placed between the cathode and anode to avoid physical contact of the electrodes; at the same time it provides a channel for the transportation of lithium ions through its micro-nano pores during charging and discharging of the battery. To date, monolayer and triple-layered polyolefin-based separators have been used most commonly in LIBs. Initially, separators were studied only in the context of improving the safety properties and high-temperature performance of the cells [47, 48]. In an LSB, however, the micro-nano pores responsible for the passage of lithium ions also act as a corridor for dissolved lithium polysulfides. Moreover, these polyolefin-based separators have a hydrophobic surface, which seriously affects their ability to retain electrolyte solutions. To overcome this problem, the focus has been shifted recently from modification of the cathodes to modification of the separators. Strategies that have been employed to modify the surface of the separator have involved using various polymers for higher electrolyte intake [49-52] and various carbon coatings to entrap the lithium polysulfides on the cathode side and, thereby, stop the shuttling phenomenon [53-55]. Herein, we report a novel approach of using a bifunctional separator—formed by spray-coating poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) on top of the separator—that is not only a facile and effective method for suppressing the shuttling mechanism of lithium polysulfides but also modifies the surface of the separator from hydrophobic to hydrophilic, resulting in greater wettability, enhanced electrolyte intake, and increased electrochemical performance. This simple strategy greatly enhanced the cycling stability of LSBs, with losses as low as 0.0364% per cycle for 1000 cycles at a low C-rate of 0.25. To the best of our knowledge, the LSB described herein has the lowest-reported degradation rate per cycle at a low C-rate.

Experimental section

Sample Preparation

Celgard 2500 was used as received as the cell separator. Bifunctional separators were prepared by mixing PEDOT:PSS (Clevios PH1000; PEDOT:PSS concentration: 1.3% by weight; weight ratio of PSS to PEDOT: 2.5) with ethanol (1:5, vol%) and then spray-coating onto one side of Celgard separator. Coatings were applied at 0.025, 0.07, and 0.25 mg cm⁻².

Characterization

The morphologies of the samples and energy dispersive X-ray spectroscopy (EDS) were performed using an FEI Nova 200 scanning electron microscope (2–10 kV). Powder X-ray diffraction (XRD) patterns of the S-G composites were obtained using a Rigaku D/Max 2550 VB/PC X-ray diffractometer using Cu (K α) radiation, with 2θ angles recorded from 10–80°. The sulfur ratio in the S-G composite was calculated through thermogravimetric (TG) analyses performed under N₂ using a PerkinElmer TGA-7 TG analyzer. Absorption spectra of electrolytes containing lithium polysulfides were measured using a JacobsV-670 UV–Vis spectrophotometer.

Electrochemical Measurements

Sulfur-expanded graphene (S-G) samples prepared at various combinations were mixed with carbon black (super p) and poly(vinylidene fluoride) (PVDF) binder at a 80:10:10 wt% ratio to form slurries that were coated homogeneously onto Al foil current collectors. The electrodes were dried for 12 h at 50 °C under vacuum and then cut in to circular disks (diameter: 12 mm). The typical loading of sulfur was 0.9–1.1 mg cm⁻². CR2032 coin cells were prepared using lithium metal foil as the counter electrode. The electrolyte used was 1 M

bis(trifluoromethane)sulfonamide lithium (LiTFSI) in dimethoxyethane (DME) and dioxolane (DOL) (1:1, v/v) with 1 wt% LiNO_3 as an additive. Porous Celgard 2500 PP/PE pristine and bifunctional (PEDOT:PSS) coated separators was used as separators. The coin cells were assembled in an Ar-filled glove box. The electrolyte volume added to each cell was 30 μL . The galvanostatic charge/discharge was measured using a battery tester (AcuTec Systems, Taiwan) with a voltage window of 2.8–1.5 V and every cell was activated at low 0.05C for couple of cycles before testing at various C-rates. The electrochemical impedance (frequency 0.01–100,000 Hz; amplitude: 5 mV) was measured using a CHI 440 analytical system (CH Instruments).

Fabrication of Flexible Batteries

Flexible batteries were fabricated using our expanded graphene/sulfur cathode, a PEDOT:PSS-coated PP/PE separator, and Li metal as the counter electrode. An organic electrolyte was prepared by dissolving 1.0 M LiTFSI and 0.1 M LiNO_3 in a mixture of DME and DOL (1:1, v/v). Nylon and Al films (Dai Nippon Printing) were used as packing covers for the flexible batteries.

Preparation of Li_2S_6 Electrolyte

A lithium polysulfide solution was prepared by mixing appropriate ratios of sulfur powder and Li_2S in DOL/DME (1:1, v/v) solution for 24 h.

Polysulfide Diffusion Measurements

A schematic representation of the experimental setup for measuring the polysulfide diffusion is displayed in Figure. S9. A 0.5-mL solution of Li_2S_6 in DOL/DME (1:1, v/v) was placed in a transparent glass tube; the opposite end of the separator was filled with pristine DOL/DME. During the experiment, the apparatus was rested, without any movement, to exclude any influence on the diffusion behavior.

Results and discussion

In an LSB, the charging and discharging process is hampered by the poor electronic conductivity of sulfur. To make an effective cathode for an LSB, we used a novel one-step method to prepare sulfur-impregnated expanded graphene. In a typical process, the impregnation of sulfur in the expanded graphene was performed using a melt-diffusion method (Figure 1a). First, various weight ratios of commercial non-expanded graphene (Homytech) and sulfur (1:2, 1:4, 1:8, 1:12) were mixed in a sealed Teflon container and then heated at 320 °C for 4 h. The sulfur began to melt at 115 °C, while the non-expanded graphene began to expand at 300 °C. The graphene sheets were loosely stacked or folded together to construct interconnected macro pores. The sulfur vapor diffused into the voids of the graphene as it began to expand, forming polycrystalline sulfur on the graphene surface as it cooled down.

Figure 1 (a) Photograph of (a1) sulfur/non-expanded graphene and (a2) sulfur/expanded graphene (before and after hydrothermal melt diffusion process, respectively) and (a3) schematic representation of the entrapment of sulfur in the expanded graphene network in a Teflon autoclave. (b) Schematic representation of the spraying process and corresponding cross-sectional image of PEDOT:PSS on the separator; scale bar: 1 μm (c) Theoretical mechanism of a Li-S cell featuring a PEDOT:PSS-coated separator and a sulfur-infused expanded graphene cathode.

A hollow structure provides a large space for sulfur expansion during cycling. Because lithium can readily penetrate the thin carbon wall, rapid ionic transport is also possible. To confirm the presence of carbon and sulfur, we performed energy-dispersive X-ray spectroscopy (EDS) mapping; a corresponding SEM image is provided in (Figure S1). Carbon and sulfur signals were detected uniformly over the whole cross-section, indicating that sulfur was

distributed well within the hollow nanostructure. The SEM images in Figures S1 and S2 reveal, however, that the sulfur covered not only the inner pores of the expanded graphene network but also the outer surface of the graphene sheets. This outer polycrystalline sulfur would react with Li and the resultant lithium polysulfides would be free to diffuse to the anode. Supplementary Figures S3 and S4 provide a detailed analysis of the XRD and TGA data and the electrochemical performance, respectively, of the cells.

A routine separator in lithium–sulfur cells is made of Celgard (PP/PE), which maintains the ionic pathway and blocks the migration of electrons between the cathode and anode. In such separators, however, lithium polysulfides are free to shuttle between the cathode and anode, due to the porous nature of the pristine separator. In contrast, our novel PEDOT:PSS-PP/PE bifunctional separator features an abundance of sulfonate functional groups (from PSS); we suspected that these negatively charged units would effectively suppress the shuttling of soluble lithium polysulfides (S_n^-) through mutual coulombic repulsion [56]. As a result, the hopping of dissolved lithium polysulfides through the separator might be curtailed when using this bifunctional separator. On the other hand PEDOT also provides chemical interactions and forms chelated coordination structure with insoluble lithium polysulfides (Li_2S : 1.08eV, Li_2S_2 : 1.12eV) due to presence of strong electronegative atoms (S and O) in PEDOT[57-59]. From the perspective of ionic conductivity, the PSS used as a dopant in PEDOT:PSS can effectively provide Li^+ ion conductive routes and a “polar solvent–philic” environment [60]. The ionic (lithium) conductivity in PEDOT:PSS has been estimated to be on the order of $10^{-6} S cm^{-1}$ [61, 62]. Despite PEDOT:PSS not allowing very high ionic transport, it has been speculated that a nanoscale-thick PEDOT:PSS coating layer would be too thin to slow down the overall kinetics of

the electrochemical process, as we observed in previous results [60, 63, 64]. We formed a conformal layer of PEDOT:PSS with a coating of 0.07 mg cm^{-2} by spray-coating onto the pristine separator; a cross-sectional image of the bifunctional separator revealed (Figure 1b) the thickness of the PEDOT:PSS film to be approximately 800 nm.

Our S-G(4:1) device performed the best among the various combinations of sulfur/expanded graphene when tested at 0.25 C (Figure S4). Accordingly, to examine the effect of the bifunctional separator, we coupled this S-G(4:1) sample with the bifunctional separator and tested both samples at the same current density of 0.25 C for 1000 cycles (Figure 2a). The initial capacity of S-G(4:1) with a pristine separator was 981 mA h g^{-1} ; it decreased to 66 mA h g^{-1} after 1000 cycles. Thus, only 6.72% of the original capacity was preserved, providing a decay rate of 0.0932% per cycle. In contrast, the use of the bifunctional separator improved the cycling stability significantly: the initial capacity decayed from 985 mA h g^{-1} to 626 mA h g^{-1} at a decay rate of 0.0364% per cycle. The total decay from the original capacity over 1000 cycles was 36.4% (see dashed line in Figure 2b); the average coulombic efficiency was greater than 92% (Figure 2a). We attribute the high decay rate in the initial cycles of the S-G(4:1) sample when using the pristine separator to the combined effects of rapid irreversible loss of the active material (due to the shuttling phenomenon) and formation of solid electrolyte interface (SEI). In contrast, the decay in the S-G(4:1) sample featuring the bifunctional separator was more consistent throughout the 1000 cycles because of the ceased migration of lithium polysulfides during the discharge process. As a result, the bifunctional separator functioned effectively to suppress the diffusion of lithium polysulfide anions through the separator, minimizing the reaction of lithium polysulfides with lithium metal that leads to anode degradation [39, 65].

Nevertheless, a continuous decay in capacity observed, presumably because of the non-conductive nature of Li_2S and Li_2S_2 resulting in irreversible deposition.

Figure 2 (a) Cycling performance of S-G(4:1) and S-G(4:1) cells featuring the bifunctional separator, over 1000 cycles at 0.25 C (1 C = 1675 mA g⁻¹) in the voltage range 1.5–2.8 V. (b) Capacity decay percentages of the bifunctional and pristine separators. (c) Charge/discharge profiles at the 1st, 200th, 400th, 600th, 800th, and 1000th cycles when using the bifunctional separator. (d) Discharge capacities at various current densities. (e) Charge/discharge profiles of cells featuring the bifunctional separator at different C-rates.

The amount of PEDOT:PSS loaded played a critical role in the electrochemical performance of the battery. A low amount of coating (0.025 mg cm⁻²) could not form a complete compact film on the pristine separator as revealed in the SEM image (Figure S5b), ultimately having limited effect on the electrochemical performance of the LSBs, (Figure S6b). On the other hand, a thick (0.25 mg cm⁻²) of PEDOT:PSS was also applied and cycle performance was assessed (see cycle life data in Figure S6a). The low capacity achieved in case of 0.25mg/cm² coating can be attributed to higher polarization suffered by the lithium ions, As discussed before PEDOT:PSS film doesn't offer high lithium ion conductivity (10⁻⁶ S cm⁻¹), therefore it is believed that the thicker coating of PEDOT:PSS on top of separator can retard the diffusion of lithium ions resulting in lower capacity and higher polarization. Figure. 2c presents the voltage profiles of the pristine and bifunctional separator at the 1st, 200th, 400th, 600th, 800th, and 1000th cycles. We observe two distinct discharge plateaus at 2.3 and 2.05 V; the higher-voltage plateau corresponds to the transformation of molecular S₈ to a series of soluble polysulfides (Li₂S₈–Li₂S₄), while the lower corresponds to the transformation of Li₂S₄ to insoluble Li₂S₂ and Li₂S.

We conducted further tests on the rate capability to compare the performance of the bifunctional and pristine separators (Figure 3d). Subsequent cycles at 0.1, 0.5, 1, and 2 C revealed capacities of 1260, 928, 783, and 751 mA h g⁻¹, respectively, for the bifunctional separator. When we discharged the bifunctional separator again at 0.1 C, we achieved a

reversible capacity of 1020 mA h g⁻¹ (i.e., 80.9% of the original capacity), suggesting great stability at different C-rates. The pristine separator provided values of 1265, 857, 747, and 690 mA h g⁻¹, respectively, at 0.1, 0.5, 1, and 2 C; when the current was switched abruptly from 2 to 0.1 C, a reversible capacity of only 881 mA h g⁻¹ was recovered only 69.6% of the original capacity. We attribute the better rate performance of the bifunctional separator to effective suppression of the dissolution of polysulfides.

We used EIS spectroscopy to gain additional insight into the effect of the PEDOT:PSS coating on top of the separator. These tests were conducted using freshly prepared cells incorporating the bifunctional and pristine separators. The Nyquist plots of these electrodes displayed a single depressed semi-circle in the high- and medium-frequency range and an inclined line in the lower-frequency region (Figure 3), associated with charge transfer resistance (R_{ct}) and Warburg impedance (W_0) [66, 67], respectively. The higher frequency intercept (on the left-hand side) corresponds to the bulk resistance (R_s) of the cell, including the electrode and electrolyte resistances [68]. The value of R_{ct} for the cell featuring the bifunctional separator (151 Ω) was less than that (176 Ω) detected for the cell containing the pristine separator; similarly, the value of R_s of the cell featuring the bifunctional separator (4.50 Ω) was lower than that (4.76 Ω) for the cell incorporating the pristine separator. We ascribe the decreases in the values of R_{ct} and R_s to increased electrolyte retention within the separator, due to hydrophilic PEDOT:PSS surface; similar results, based on polymer coatings on the separator, have been reported previously [50, 69]. A simple wetting test was performed to verify the hydrophilic character of bifunctional separator as shown in the (Figure S7). After dropping an organic electrolyte [8 μ l of 1.0 M LiTFSI and 0.1 M LiNO₃ in a mixture of DME and DOL (1:1, v/v)] on top of separator,

the droplet can wet the bifunctional separator (right) much better the pristine separator (left) as shown in (Figure S7b).

To assess whether the bifunctional separator enhanced the retention of dissolved lithium polysulfide species, we conducted a simple, but informative, polysulfide diffusion experiment using the setup displayed in (Figure S9). As expected, the pristine separator could not bind the lithium polysulfides, with the color of DOL:DME changed from colorless to brownish-red after 60 min of rest (Figure 4a) [70]. In contrast, the bifunctional separator (PEDOT:PSS loading: 0.07 mg cm^{-2}) suppressed most of the polysulfide diffusion. Even after 60 min, no visual change of color DOL:DME was detected pertaining to effective shield formed by PEDOT:PSS against polysulfide diffusion. However, after 180 min small proportion of lithium polysulfides do penetrate through the pristine separator. In addition, we performed the UV–Vis absorption spectra (Figure 4b) after 60 min for solution obtained from pristine separator (with suitable dilution to allow the absorbance to reach an appropriate range). The DOL:DME solution obtained from the pristine separator yielded a peak near 615 nm, corresponding to the diffusion of short-range polysulfides (e.g., S_3^{2-}) in the solution, as well as a peak near 450 nm, corresponding to the presence of long-range polysulfides (e.g., S_6^{2-}) [71-73].

Figure 3 Electrochemical impedance spectra of pristine and bifunctional separators in freshly prepared cells.

Figure 4 (a) Polysulfide diffusion test of (top) untreated Celgard and (bottom) bifunctional separator. (b) UV-Vis absorbance spectra revealing the diffusion of lithium polysulfide in DOL:DME solution using pristine separator after 60 min; inset: solution obtained from the pristine separator.

We also tested the cell performance at a high current density of 0.5 C for the systems incorporating the pristine and bifunctional separators (Figure S8a). The cell featuring the pristine separator did not function effectively, due to free shuttling of polysulfides, higher polarization, and lower sulfur utilization; the cell incorporating the bifunctional separator displayed much better performance. Similarly, we also tested the cells containing bifunctional and pristine separators at a lower current density of 0.1 C (Figure S8b). Once again, the cell assembled with the bifunctional separator displayed far superior performance, confirming that the PEDOT:PSS bifunctional separator improved the cycling stability at various C-rates. Meanwhile, coating PEDOT:PSS on top of membrane is facile and efficient way to build an electrostatic shield in order to stop the diffusion of lithium polysulfides. Other methods, like coating directly on top of cathode yields worse performance as compared to separator coating. This can be associated to breakage of PEDOT:PSS layer during volume expansion of cathode while charging/discharging the battery and non-uniform PEDOT:PSS coated layer due to porous nature of cathode as shown by cycling data in (Figure S10).

To demonstrate a flexible LSB based on an S-G cathode, we fabricated a device featuring a bifunctional separator and commercial lithium metal as the anode. Figure 5a displays an open-circuit voltage of 2.34 V, the theoretical value for an LSB. Upon bending, there was no change in the open-circuit voltage (Figure 5b); under the same bending conditions, a green LED was lit up once it was connected to the flexible battery. Furthermore, the adhesion of the bifunctional separator to the PEDOT:PSS was stable at the separator surface; thus, our bifunctional separator exhibited good flexibility with no peeling off under the folded conditions (Figure 5d). The Li-S cell with bifunctional separator after running for 300 cycles was disassembled for further investigation; the SEM image of the cycled separator (Figure S12) reveal no indication of any

critical damage. Table 1 compares the cyclic stabilities of other reported modified bifunctional separators in LSBs; our present bifunctional separator has far superior performance in terms of stability, with a very low decay rate.

Figure 5 (a, b) A flexible battery using an S-G cathode, a bifunctional separator, and Li metal as the anode at different bending angles. (c) An LED lit up by the flexible battery. (d) Flexibility test of the bifunctional separator (without peeling).

Table 1
Cycling stabilities of LSBs featuring modified separators

Type of coating on to PP/PE separator	Initial discharge capacity (mA h g ⁻¹)	Final discharge capacity (mA h g ⁻¹)	Current density (mA h g ⁻¹)	Number of cycles	Degradation rate per cycle (%)	S loading (mg cm ⁻²)	S content (wt %)	Ref.
Graphene coating	1000	680	1 C	300	0.106	3–4	–	[67]
Carbon black coating	1306	810	0.5 C	200	0.19	1.1–1.3	55	[74]
Microporous carbon coating	1214	503	0.2 C	500	0.117	2.0	65	[75]
Microporous/PEG coating	1307	596	0.2 C	500	0.109	2.0	65	[75]
MWCNT coating	1073	621	1 C	300	0.14	2.0	65	[53]
PVDF KOH activated CB	1150	669	0.5 C	500	0.084	7.0	70	[76]
PVDF CB coating	1350	740	0.2 C	500	0.09	1.5–2	50	[77]
Meso carbon coating	1060	683	1 C	500	0.071	1.5–1.6	50	[54]

PEDOT:PSS coating	914	682	0.25 C	1000	0.0364	0.9– 1.1	64	This paper
PEDOT:PSS coating	901	596	0.5 C	500	0.067	0.9– 1.1	64	This paper
PEDOT:PSS coating	748	481	1 C	500	0.0714	2.9	64	This paper

Conclusion

The performance of LSBs is vastly improved upon the introduction of a bifunctional separator, prepared through spraying with PEDOT:PSS. The unique bifunctional PEDOT:PSS/separator design substantially decreases lithium polysulfide permeation—a significant improvement over the pristine separator (porous Celgard) in terms of suppressing soluble lithium polysulfide shuttling and the cycle life of LSBs. Batteries incorporating the bifunctional separator displayed extraordinary cycling performance, with decay rates as low as 0.0364% per cycle over 1000 cycles; rate capability tests revealed a remarkable capacity retention of 80.9% when the current was switched from 2 to 0.1 C. We also prepared a functioning flexible battery featuring a sulfur-expanded graphene composite cathode and a bifunctional separator, emphasizing the suitability

of our design in flexible power sources. , Moreover this approach of bifunctional separator can also be applied in other Li ion batteries, Li air batteries and super capacitors systems where the electrolyte intake is less due to hydrophobic nature of the separator, as well as in the field of Li–selenium batteries, where shuttling of polyselenides is a big issue responsible for capacity decay.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version

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