

Conductive Polymer-Based Interlayer Modified Separators in Lithium–Sulfur Batteries

Subjects: Polymer Science

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Lithium–sulfur batteries (LSBs) are considered a promising candidate for next-generation energy storage devices due to the advantages of high theoretical specific capacity, abundant resources and being environmentally friendly. However, the severe shuttle effect of polysulfides causes the low utilization of active substances and rapid capacity fading, thus seriously limiting their practical application. The introduction of conductive polymer-based interlayers between cathodes and separators is considered to be an effective method to solve this problem because they can largely confine, anchor and convert the soluble polysulfides.

Keywords: lithium–sulfur batteries (LSBs) ; conductive polymer ; interlayers ; PPy ; PANI ; PEDOT ; PSS

1. Introduction

Lithium–sulfur batteries (LSBs) are considered one of the most promising energy storage devices due to the advantages of high theoretical specific capacity, resource abundance and low toxicity. However, the severe diffusion of polysulfides during repeated charging/discharging leads to the low utilization of active materials, corrosion of lithium anode and large polarization of sulfur cathode, and seriously limits their practical application [1][2][3][4][5][6][7][8]. In this regard, plenty of work has been carried out to suppress the diffusion of polysulfides in LSBs [9][10][11][12][13][14], such as the design of host materials [4], the introduction of interlayers between cathodes and separators [15][16][17][18][19] and the optimization of electrolytes [20][21]. Specifically, the introduction of interlayers between cathodes and separators is considered a promising approach because it can obviously suppress the shuttle of lithium polysulfides, and the preparation method is simple and easy to scale-up [22][23]. In the past few years, pure carbon materials [15], pure conductive polymers [24], metal foam foil [16], metal compounds [25][26][27], carbon-based materials [28][29] and conductive polymer-based materials [30][31] have been employed as interlayers by scientists. Among them, conductive polymers have more advantages of excellent conductivity, strong polysulfide adsorption capacity, moderate mechanical strength and porous structure [31][32]. In addition, some conductive polymers are electrochemically active and can contribute capacity to offset the reduction of gravimetric energy density caused by the addition of interlayers [33]. In 2015, Ma et al. first inserted polypyrrole (PPy) nanotube film between the cathode and the separator. The first discharge capacity of the as-assembled LSB could reach 1102 mAh g⁻¹, and a high retention rate of 64% was obtained after 300 cycles at 0.5 C [24]. Moon et al. synthesized a highly uniform polyaniline (PANI) film on the sulfur cathode by a transfer printing method. The battery with the printed PANI layer showed a high capacity retention of 96.4% after 200 cycles at 1 C [34]. Although achievements have been made during the past few years, there is still no special report on the research progress of conductive polymer-based interlayers.

A free-standing interlayer normally needs a certain thickness to allow it to support itself, which reduces the gravimetric energy density, and the solid–solid interfacial contact between interlayer and separator/sulfur cathode is insufficient. Separators, mainly composed of polymer films with many voids, are one of the most important parts of LSBs to prevent direct contact and short circuit between the cathode and anode. However, the commonly used polymer film has no functional groups to select ions. Soluble polysulfides can easily pass through the voids of the separators to reach the lithium anode, causing a large loss of active materials [35][36]. Conductive polymer-based interlayers with imine or conjugated structures can greatly chemisorb polysulfides and limit their diffusion [37]. If the separator is modified with conductive polymer-based materials, soluble polysulfides can be effectively captured, fixed and converted, and thus improve the cycling performance of the battery (or reduce the shuttle effects of polysulfides) [38][39].

2. PPy-Based Material Modified Separators

PPy has good affinity with electrolytes and strong adsorption capacity for polysulfides and can also contribute to the capacity. These outstanding advantages of PPy enable it to be extensively used in the modification of separators in LSBs

[40][41]. Ma et al. used PPy nanotubes, PPy nanowires and reduced graphene oxide (rGO) to modify the separators. They found that the diffusion of polysulfides was inhibited and the utilization of sulfur cathode was improved. Attributed to the excellent affinity of PPy with lithium polysulfides and electrolytes, the PPy-modified separators showed enhanced electrochemical performance in LSBs. After 200 cycles at 0.2 C, the discharge capacity of the LSB without separator modification was only 215 mA h g⁻¹ and the coulomb efficiency was less than 80%. In contrast, the discharge capacity of the batteries with PPy nanotubes and PPy nanowire modified separators was up to 865.4 mA h g⁻¹ and 832.1 mA h g⁻¹, with the corresponding coulomb efficiency of 89.4% and 88.1%, respectively [42]. In addition, Li et al. designed a PPy nanofiber-coated separator and assembled it into flexible LSBs. The PPy nanofiber-coated separator could successfully suppress the diffusion of soluble polysulfides, and could also be used as an upper collector. The kinetic speed of the electrochemical reaction was significantly accelerated. PPy had electrochemical activity, which could provide part of the capacity. Combined with the improved sulfur cathode, the initial specific capacity of the LSB was as high as 1064 mA h g⁻¹, and after the 20th charge/discharge cycle at 0.1 C, the capacity could still be maintained at a high value of 848 mA h g⁻¹ [33].

In addition to PPy nanotubes, PPy nanowires and PPy nanofibers, PPy spheres have also been applied to modify the separators. Li et al. successfully prepared a new layered porous PPy sphere to modify the separator. When PPy sphere slurry was coated on the separator, the polarization of the cathode could be significantly reduced, and polysulfides could be effectively suppressed, thus significantly improving the sulfur utilization rate. The modified separator was assembled into LSBs. After 100 cycles at 0.2 C, the capacity was 855 mA h g⁻¹, and the capacity was 507 mA h g⁻¹ after discharge at 3 C [43].

Other than coating PPy on one side of the separator close to the cathode, Li et al. coated PPy on both surfaces of the commercially available separator by in situ gas phase polymerization. By using this separator, electrolyte absorption was enhanced, and the shuttle effect was inhibited, thus improving electrochemical performance. With this double-sided coating separator, the capacity decay rate was only 0.083% per circle after stable circulation for 250 cycles at 0.5 C. The cycle performance was also excellent at higher area capacity (4.8 mA h cm⁻²); after 150 cycles at 0.2 C, the capacity retention rate kept up to 75.6% [44]. Similarly, Fu et al. also fabricated a dual-functional separator with PPy coating on both surfaces by a vapor-phase polymerization method, which inhibited the shuttle of polysulfides. The separator was assembled into LSBs with excellent electrochemical performance; for example, the decay rate of 500 charge/discharges at 1 A g⁻¹ was only 0.037% [45].

To enhance the chemisorptive binding with polysulfides, metal oxides have also been adopted to combine with PPy in the modified separator materials to further chemisorb polysulfides. For instance, Yin et al. prepared a PPy/ZnO modified separator to anchor polysulfides. Due to the existence of ZnO and PPy, the PPy/ZnO interlayer could prevent the migration of soluble polysulfides and greatly improve the performance of LSBs. After charging/discharging for 100 cycles at 0.2 C, the battery retained a high specific capacity of 579 mA h g⁻¹ [46]. Moreover, Ma et al. synthesized a NiCo₂O₄@PPy multifunctional interlayer. Flowery NiCo₂O₄ and PPy could physically adsorb, chemically anchor and further accelerate the transformation of polysulfides. The initial capacity of the battery could reach 1588 mA h g⁻¹ at 0.1 C discharge, and the average coulomb efficiency was 95.2%. At 2 C, the discharge-specific capacity was also up to 740 mA h g⁻¹. After 400 cycles of charging and discharging, a capacity decay rate of 0.107% could be obtained [47].

Besides chemical anchor of polysulfides by combining metallic oxides with PPy, physical confinement by carbon materials with PPy can also be used to capture polysulfides. Zhou et al. developed a PPy/graphene composite interlayer, which could inhibit the dissolution of polysulfides and improve the conversion and utilization of sulfur cathode. As a result, the initial specific capacity of LSBs was as high as 1443 mA h g⁻¹. When charged and discharged 1000 times, it could maintain 0.04% capacity decay rate per cycle at 1 C [48].

3. PANI-Based Material Modified Separators

PANI has the characteristics of high ionic conductivity and a large void ratio, which could be employed to modify separators [49][50][51]. The modified separator could suppress the shuttle of polysulfides and reduce the surface impedance of the separator, while the inherent pore structure of the separator was barely affected [40][52]. For example, Tubtimkuna et al. presented hydrolyzed polyethylene grafted PANI via amide coupling reaction as a modified separator. This separator could effectively inhibit the diffusion of polysulfides through the amine group of PANI. This separator not only improved the specific capacity, but also inhibited the capacity attenuation [53].

In contrast to pure PANI, combining carbon materials with PANI as interlayers can further capture polysulfides. Chang et al. prepared a modified separator composed of PANI nanofibers/MWCNT. The PANI coating could be tightly combined on

the commercial separator, which was highly effective in capturing the diffused polysulfides. This was mainly attributed to the strong chemical interaction of sulfur-containing species and the imine group ($-N=C$) from the quinone ring. When the modified separator was assembled into a battery, the initial discharge capacity reached 1020, 867 and 791 mA h g⁻¹ at 0.2 C, 0.5 C and 1 C, respectively [54]. Shi and co-workers prepared a separator modified by MWCNT/PANI sulfide, which could selectively control the migration of Li⁺ and inhibit the diffusion and shuttle of polysulfides. Therefore, even at high sulfur loading (5 mg cm⁻²), the LSBs assembled by this separator still exhibited excellent electrochemical performance, and the reversible capacity was up to 1078 mA h g⁻¹, which was better than the performance of a pure separator and an MWCNT modified separator [55].

In addition to physical absorption of polysulfides by carbon materials, a chemical anchor was also used to capture polysulfides. Chen et al. modified amorphous vanadium pentoxide (V₂O₅) nanowires encapsulated in PANI onto commercial polypropylene separators. When the separator was assembled into LSBs, it had higher electrochemical performance than the single-component modified separator. The adsorption test showed that the adsorption capacity of V₂O₅·nH₂O@PANI towards Li₂S₆ was stronger, mainly due to the positive synergy between V₂O₅·nH₂O and PANI [56]. To physically absorb and chemically anchor the polysulfides, Archer and collaborators applied Langmuir–Blodgett scooping coating technology to prepare an MWCNT/TiO₂ nanoparticle/PANI interlayer. MWCNT physically blocks polysulfides, while PANI and TiO₂ nanoparticles can chemically adsorb polysulfides. Under different discharge rates, the battery can also show higher capacity and better cycle performance [57]. Besides physical absorption and/or chemical anchor of polysulfides, the catalytic effect of interlayer can be largely improved. Jo et al. reported a hollow Co-Fe Prussian blue analogue encapsulated by PANI, and coating PANI on the prepared hollow Co-Fe Prussian blue could improve the catalytic effect and enhance the conductivity. After 100 charging/discharging cycles at 1 A g⁻¹, the capacity retention rate was as high as 83.5%, with an average coulomb efficiency of 99.5% [58].

4. PEDOT: PSS-Based Material Modified Separators

PEDOT is a polythiophene derivative with high conductivity, excellent chemical stability and flexibility, which can inhibit the shuttle of polysulfides and accelerate the electron transfer speed, further improving the energy density and cycle stability of LSBs [59][60][61]. Within separators modified by PEDOT, the electrochemical performance of LSBs can be significantly improved [40][62][63][64]. For example, Abbas et al. reported a separator that was mainly composed of PEDOT: PSS sprayed onto the commercial separator. The negatively charged SO₃⁻ in PSS could electrostatically shield the soluble polysulfides, and the O, S atoms in PEDOT could chemically interact with low-order polysulfides to prevent them from passing through the separator. When the LSB was assembled and charging/discharging was repeated 1000 times at 0.25 C, the attenuation rate was as low as 0.0364% per cycle [65]. With the help of electrostatic layer-by-layer self-assembly strategy, Shi and co-workers integrated PEDOT: PSS and a functional covalent triazine framework (CTF) to develop a layer-by-layer separator. Functional CTF with high porosity and lithiophilicity improved the chemical adsorption capacity for lithium polysulfides, thus the polysulfide shuttle was inhibited and the utilization rate of active sulfur material was improved. During 1000 cycles of charging and discharging at 1 C, 0.052% capacity attenuation and sulfur utilization rate was still 90.7% at 0.1 C [66].

Due to the advantages of being highly conductive and lightweight, etc., carbon materials were further combined with PEDOT: PSS to decorate the separators. For instance, Yi and his colleagues prepared a separator coated with carbon black/PEDOT: PSS. It could effectively inhibit polysulfides and significantly accelerate Li⁺ migration. When assembled into LSB, the specific capacity was up to 1315 mA h g⁻¹ after 1100 charges/discharges at 0.2 C, and the discharge capacity was still up to 699 mA h g⁻¹ at the current density of 2 C, indicating the excellent electrochemical performance, which was better than that of the LSB without an interlayer [67]. Lee et al. prepared a PEDOT: PSS/rGO composite as the coating material modified on the separator. PEDOT: PSS/rGO was well-combined with the separator to physical adsorption and chemical anchor polysulfides to prevent the shuttle effect. After 100 charging/discharging at the rate of 0.5 C, the retained capacity was still as high as 800 mA h g⁻¹, which was more than twice that of the LSB without an interlayer [68].

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