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Short Communication

Polyelectrolyte Self-assembled Modified Ceramic Membrane and its Application in Lithium-Sulfur Batteries

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As one of the candidates for lithium-ion batteries, lithium-sulfur (Li-S) batteries have received extensive research and attention. However, the shuttle effect of soluble lithium polysulfide has hindered the commercial application of Li-S batteries. Therefore, this paper proposes the use of a polyelectrolyte self-assembled modified ceramic separator to inhibit the shuttling of lithium polysulfide intermediates. First, a layer of silica was applied on the surface of a polyethylene (PE) separator. Then, polyethyleneimine (PEI), polyacrylic acid (PAA), polydiallyldimethylammonium chloride (PDDA) and sodium polystyrene sulfonate (PSSNa) were selected to synthesize two self-assembled cationic/anionic polyelectrolytes. Finally, layer-by-layer (LBL) self-assembly technology was used to grow the polyelectrolyte in situ on the ceramic separator to form a functional separator. Galvanostatic charge/discharge revealed that the LBL4-PEI-PAA separator and LBL4-PDDA-PSSNa separator have improved specific capacity and cycle performance compared to the\PE separator, and there is no obvious overcharge phenomenon when using an electrolyte without a lithium nitrate additive. In particular, the LBL4-PDDA-PSSNa separator has a first-lap discharge specific capacity of 981.8 mAh/g. The capacity retention rate is 88.9% after 100 cycles, which effectively suppresses the lithium polysulfide shuttle effect.

Keywords: lithium-sulfur battery, shuttle effect, self-assembly, cation/anionic polyelectrolytes

1. INTRODUCTION

The global energy structure is gradually shifting from fossil energy to clean and renewable energy, such as solar and wind, with the development of society. Due to its space-time characteristics, future energy sources require a safe, inexpensive and long-life electrochemical energy storage system to achieve efficient use[1-2,10]. Lithium-sulfur (Li-S) batteries have received extensive research and attention due to their rich sulfur reserves, low price, environmental friendliness and high theoretical equivalent density. The theoretical volume and mass energy density of lithium-sulfur batteries are 2800 Wh/L and 2600 Wh/kg, respectively, 7 times that of commercial lithium-ion batteries[2-5,7]. Therefore, Li-S batteries are considered lithium-ion battery candidates.

Although lithium-sulfur batteries have obvious advantages, there are still many problems with sulfur cathodes: (1) Both the active material S and the final product lithium sulfide (Li_2S) are insulators, resulting in poor electronic conductivity; (2) During charging and discharging, the difference between the density of S and Li_2S will cause a massive volume change (approximately 80%) of the electrode[11-14]; and in particular, (3) During the charge and discharge process, high-order lithium polysulfide is easily dissolved in the ether electrolyte, shuttles freely between the anode and the cathode, and reacts with the lithium metal anode to produce solid Li_2S_2 and Li_2S, which are deposited on the surface of the lithium metal anode. These issues will limit the utilization of active materials, resulting in battery self-discharge and poor cycle stability[8-9,16-21]. Therefore, it is very important to inhibit the shuttle effect of the intermediate product lithium polysulfide.

The main methods to solve the shuttle effect are as follows: sulfur cathode modification, use of an artificial SEI membrane and use of a functional separator. The "shuttle effect" is caused by soluble lithium polysulfide freely passing through the separator. Therefore, the separator can be modified to suppress the free diffusion of lithium polysulfide. At present, in lithium-sulfur batteries, some functional separators have been researched. On the one hand, studies have been based on the modification of the separator, and the use of electrostatic repulsion (Nafion sulfonate, carboxylate, $BaTiO_3$)[27,35,46], steric hindrance[29,30,34,37], and ion selectivity[33,40]effectively suppresses lithium polysulfide diffusion and improves the Coulombic efficiency. On the other hand, studies have used structural materials to modify the separator to effectively inhibit the shuttling of lithium polysulfide through physical confinement[31,32,36,39,43] and chemical adsorption (Ti_3C_2, oxygen/nitrogen-containing functional groups) of the microporous structure.[25,28,42,44]。The materials of these structures can realize electron conduction with the contact surface of the positive electrode, decrease the interface resistance on the positive electrode side, realize the secondary utilization of lithium polysulfide, and ultimately achieve the purpose of improving the cycle stability and active material utilization.

In this work, a functional separator was designed and prepared that not only reduced the shuttle effect of high-order lithium polysulfide but also effectively improved the safety performance of lithium-sulfur batteries. First, a layer of SiO_2 was applied on the surface of a polyethylene (PE) separator to obtain a ceramic separator, and then, a polyelectrolyte modified ceramic separator was obtained through self-assembly (LBL) technology[15,31,41]and in situ growth of polydopamine on the ceramic diaphragm[22-23,26,38,45,47]. Compared with ordinary PE separators, the modified polyelectrolyte ceramic separator has improved mechanical properties, thermal stability, and hydrophilicity, and there is no obvious overcharge phenomenon when using electrolytes without lithium nitrate additives.

2. EXPERIMENTAL

2.1 Preparation of the polyelectrolyte ceramic separator

First, 60 mg polyvinylpyrrolidone (PVP), 40 mg sodium carboxymethylcellulose(CMC) and 0.9 g SiO_2 powder were added into a mixed solvent of 4 ml N-methylpyrrolidone (NMP) and 1 ml ethanol. Then, the samples were sonicated for 10 min and stirred at 400 rad min^{-1} for 12 h to obtain a uniform slurry. Finally, a uniform slurry was applied on the surface of a polyethylene separator (Celgard 2400,Celgard, Inc.,USA), and after standing for 6 h (35°C) and being dried under vacuum for 12 hours at 60°C, the ceramic separator was obtained.

2.2 Preparation of the PDA-modified ceramic separator

Deionized water and absolute ethanol were mixed in a volume ratio of 1:1, and tris(hydroxy)aminomethane was added to prepare a 10 mm concentration buffer (Tris, 10 mm). A 0.1 mol/l dilute hydrochloric acid solution was used to adjust the pH of the buffer to 8.5. Finally, dopamine was added to the solution at a ratio of 2 mg/ml to make a dopamine solution.

The ceramic separator (prepared in section 2.1) was soaked in 25 ml methanol solution for 30 minutes and then added to the dopamine solution for 24 hours. The separator was removed, repeatedly rinsed with deionized water and dried under vacuum for 12 h at 60°C. The polydopamine-modified separator was obtained after rinsing repeatedly with deionized water. The solution temperature in the above process was 27°C.

2.3 Preparation of the (PEI/PAA)$_n$ and (PDDA/PSSNa)$_n$ modified ceramic separators

In this paper, an electrostatic layer-by-layer self-assembled cation/anion polyelectrolyte was used to modify the ceramic separator. The above-described PDA-modified ceramic separator (4.5 cm×8.0 cm) was placed into a positively charged polyethyleneimine (PEI) (zeta potential, 2.3 mV) solution for 10 min and then infiltrated 3 times with deionized water for 2 minutes each time. Finally, the separator was placed into a negatively charged polyacrylic acid (PAA) (zeta potential, -0.7 mV) solution for 10 minutes and infiltrated 3 times with deionized water for 2 minutes each time to obtain a single layer of LBL-PEI-PAA. The above method was repeated to obtain the desired number of layers (usually, n=2-10) and dried at room temperature to obtain the LBLn-PEI-PAA-modified ceramic separator. In the same way, the PDA-modified ceramic separator was immersed in a positively charged polydiallyldimethylammonium chloride (PDDA) (zeta potential, 5.9 mV) solution and a negatively charged sodium polystyrene sulfonate (PSSNa) (zeta potential, -0.9 mV) solution to obtain the LBLn-PDDA-PSSNa-modified ceramic separator.

2.4 Ion selective permeability performance experiment

Under the same conditions, the PE separator and LBL-PE separator were used to separate 1,2-dimethoxyethane (DME) solution and lithium polysulfide (Li_2S_8) solution separately and observe the change in the diffusion of lithium polysulfide over time in the two cases.

2.5 Material characterization

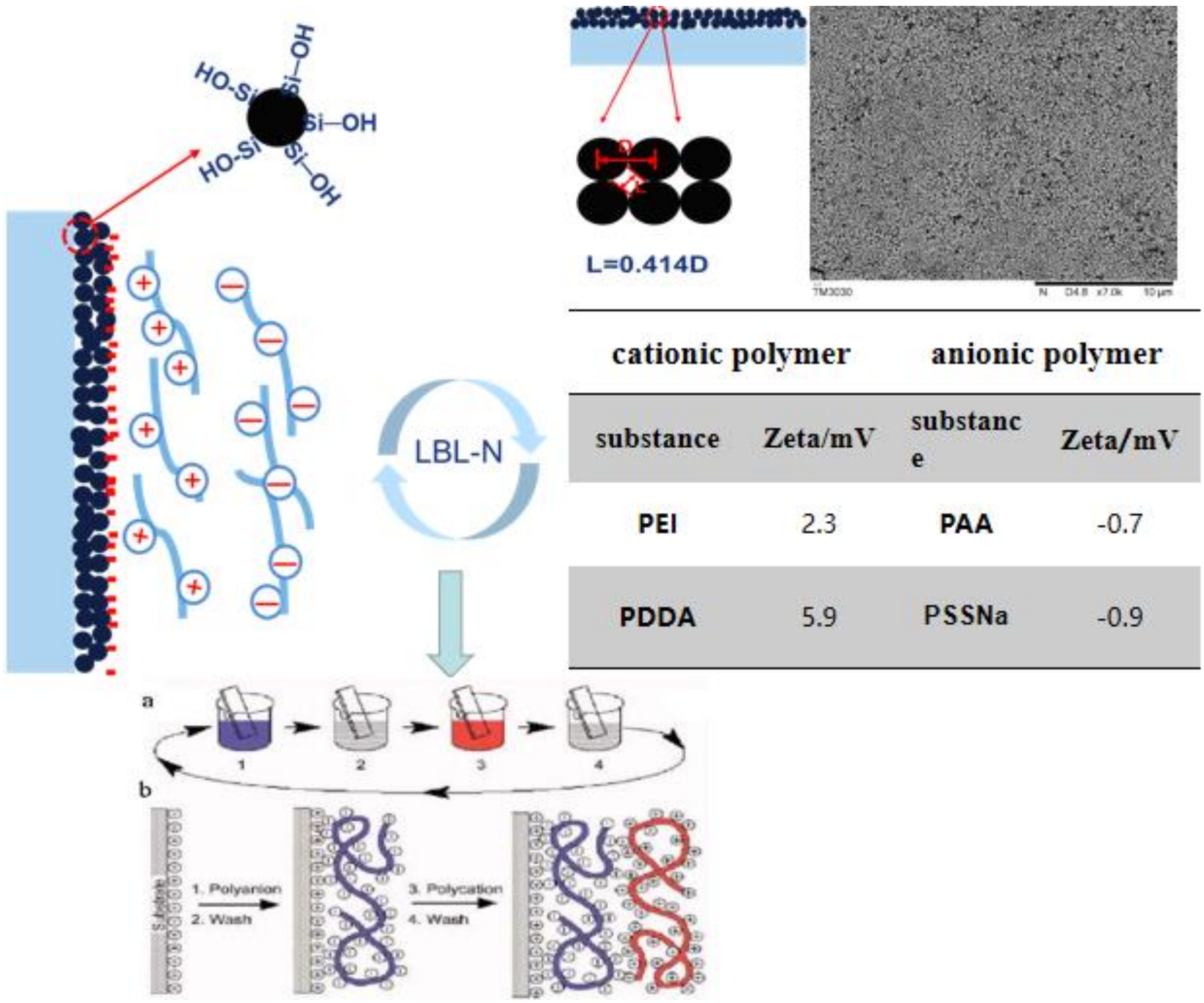
The morphology of the sample was observed by scanning electron microscopy (SEM, Hitachi S-4800). The surface elements of the sample were analysed by energy-dispersive X-ray spectroscopy.

2.6 Electrochemical measurements

A CR2016 coin cell was used for electrochemical performance characterization. Sulfur was used as the positive electrode (with a load of 1 mg/cm^2), and the electrolyte was 1 M LiTFSI in DME:DOL = 1:1 Vol% using an LBL-PE separator. Galvanostatic charge/discharge was performed at 0.2 C between 1.5 V and 3.0 V by using a battery test system (Shenzhen Xinwei New Energy Technology Co., Ltd.).

3. RESULTS AND DISCUSSION

As shown in Figure 1, by applying a layer of SiO_2 on the surface of the polyethylene (PE) separator, the particle size of SiO_2 is uniform, the gap width between the particles has a relationship of approximately $L=0.414D$, and there are a large number of silicon hydroxyl bonds (Si-OH) on the surface. The performance of ceramic separators is affected by many factors such as inorganic powders and adhesives. Organic adhesives can significantly increase the hydrophilicity of the separator and its interaction with the electrolyte, the ability to retain liquid and the ionic conductivity. However, organic adhesives can easily absorb the electrolyte to form a gel layer, which will decrease the adhesion performance between the coating layer and the separator, resulting in hidden safety risks; at the same time, the production cost of ceramic separators is high, and the process is environmentally unfriendly. Hence, in this paper, PVP and CMC are selected as composite adhesives for more effective adhesion of the inorganic powders to improve the uniformity of the ceramic separator coating. A more uniform and denser coating is considered to have higher thermal stability. The silicon hydroxyl bond has a large negative polarity, which is helpful for the selective adsorption of positively charged cationic polymers. The voids between particles and the electrostatic interaction of polyelectrolyte functional groups can inhibit the shuttle effect.



cationic polymer		anionic polymer	
substance	Zeta/mV	substance	Zeta/mV
PEI	2.3	PAA	-0.7
PDDA	5.9	PSSNa	-0.9

Figure 1. Schematic diagram of the preparation of the polyelectrolyte-modified ceramic separator.

The SEM image of the separator of LBLn-PEI-PAA and LBLn-PDDA-PSSNa cation/anion polyelectrolyte electrostatic layer-by-layer (LBL) self-assembly is shown in Figure 2. In the figure, 4 and 8 in LBL4-PEI-PAA, LBL8-PEI-PAA, LBL4-PDDA-PSSNa and LBL8-PDDA-PSSNa represent 4-layer and 8-layer self-assembled surfaces, respectively. The surfaces of the LBL4-PEI-PAA and LBL8-PEI-PAA separators have obvious gullies, and the surfaces are rough. The thickness of the separator increases as the number of layers on the membrane surface increases, and the particles will accumulate and agglomerate on the membrane surface, which gradually increases the hardness. When n=8, the separator is destroyed due to large cracks, resulting in a decrease in separation performance. For LBL4-PDDA-PSSNa and LBL8-PDDA-PSSNa, when n=4, the particle distribution on the separator surface is uniform, and the surface is smoother. As the number of layers increases to 8, the surface of the separator becomes rough, which may be due to the accumulation and agglomeration of nanoparticles on the surface of the separator. Therefore, LBL4-PDDA-PSSNa has better surface properties.

As shown in Figure 3, the element mapping diagram of the surface of the LBL4-PDDA-PSSNa separator indicates that the surface contains S, Si and N. This observation shows that the anionic polymer and cationic polymer are successfully adsorbed on the surface of the LBL4-PDDA-PSSNa separator.

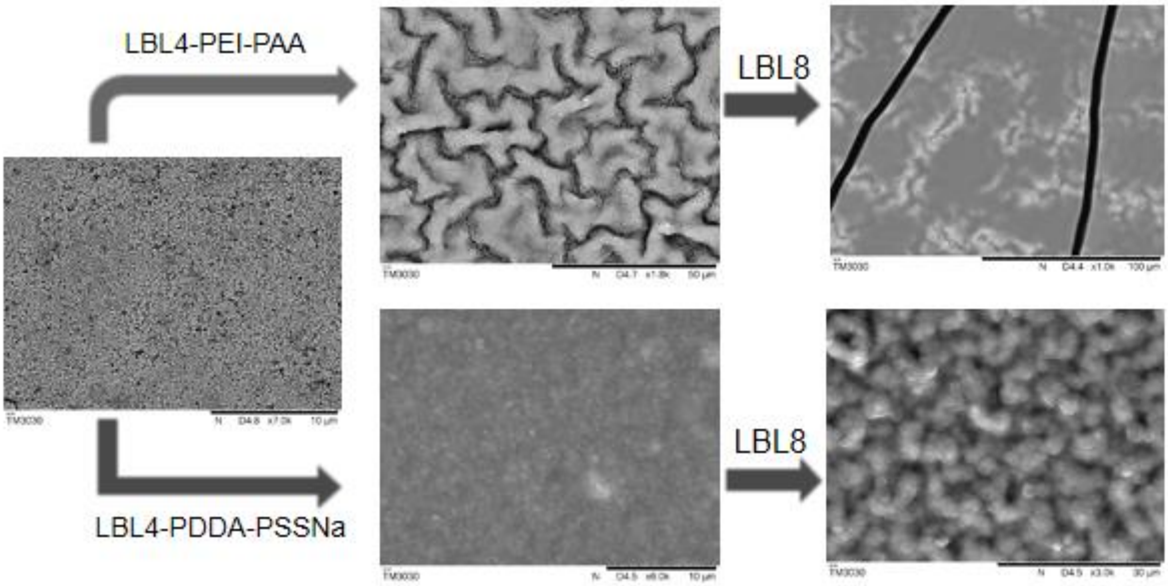


Figure 2. SEM images of the separator after electrostatic LBL self-assembly.

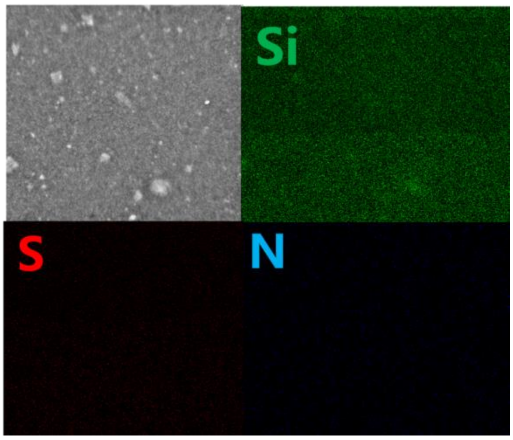


Figure 3. The element mapping diagram of the surface of the LBL4-PDDA-PSSNa separator.

Lithium polysulfide shuttling was observed at different times by the PE separator and LBL4-PDDA-PSSNa separator (Figure 4). The diffusion of lithium polysulfides is clearly observed only 2 hours after using the PE separator. However, the observation of lithium polysulfide diffusion after using the LBL4-PDDA-PSSNa separator for 24 hours is still not obvious. The key role of the polarization process in delaying the diffusion of lithium polysulfides was revealed, and the LBL-PE separator has a certain inhibitory effect on the lithium polysulfide shuttle.

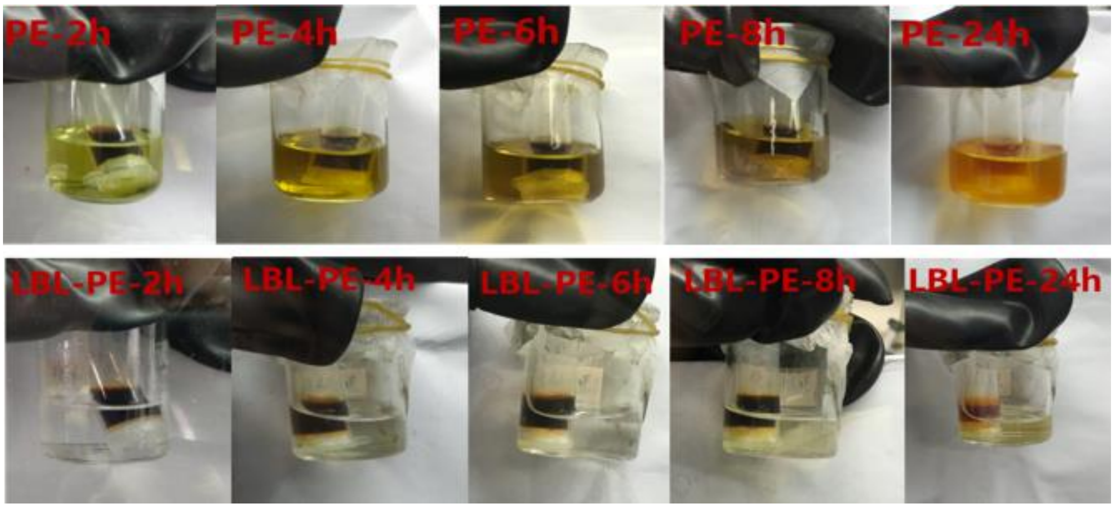


Figure 4. PS inhibition experiment of PE separator and LBL-PE separator.

The PE separator, LBL4-PDDA-PSSNa, and LBL4-PEI-PAA were used to assemble a battery for electrochemical testing, as shown in Figure 5. It is worth noting that the electrolyte used cannot have any additives (such as lithium nitrate), which can form passivation films on the surface of lithium metal. As is known, the passivation layer on the surface of lithium metal itself can inhibit the shuttle effect, so the influence of the separator on the phenomenon of lithium polysulfide dissolution cannot be evaluated if additives are added. Coulombic efficiency (CE) is a key parameter to evaluate the shuttle effect. The dissolved lithium polysulfides will cause battery self-discharge (shuttle effect), and the charge specific capacity exceeds the discharge specific capacity, causing the battery to overcharge. Because the LBL4-PDDA-PSSNa separator can effectively suppress the shuttle effect, it can be seen from Figure 5 that the cycle performance of the LBL4-PDDA-PSSNa separator is better than that of the PE separator. After 100 cycles, the capacity retention rate of the LBL4-PDDA-PSSNa separator (88.87%) is better than that of the PE separator (80.78%). The battery assembled with the LBL4-PDDA-PSSNa separator has an initial Coulombic efficiency of 99.5%, and there is no obvious overcharge phenomenon (Figure 5c). However, the initial Coulombic efficiency of the PE separator is only 33.6%, and overcharge occurs (Figure 5b). This result clearly proves that the polyelectrolyte self-assembled modified ceramic separator can inhibit the shuttling of dissolved lithium polysulfides from the anode to the cathode. The first-lap reversible capacities of PE and the LBL4-PDDA-PSSNa separator are 931.04 mAh/g and 981.77 mAh/g, respectively. The abovementioned electrochemical test results show that the LBL4-PDDA-PSSNa separator has better electrochemical performance than the PE separator. This is because the LBL4-PDDA-PSSNa separator is loaded with PSSNa, and the affinity of the LBL4-PDDA-PSSNa separator with the electrolyte has been improved, allowing the electrolyte to be more effectively adsorbed and ensuring that the electrolyte is sufficient during the battery cycle. At the same time, when the LBL4-PDDA-PSSNa separator is used, the voids between the particles and the electrostatic interaction between the polyelectrolyte functional groups can effectively inhibit the shuttle effect of lithium polysulfides, thereby improving the utilization of the active materials.

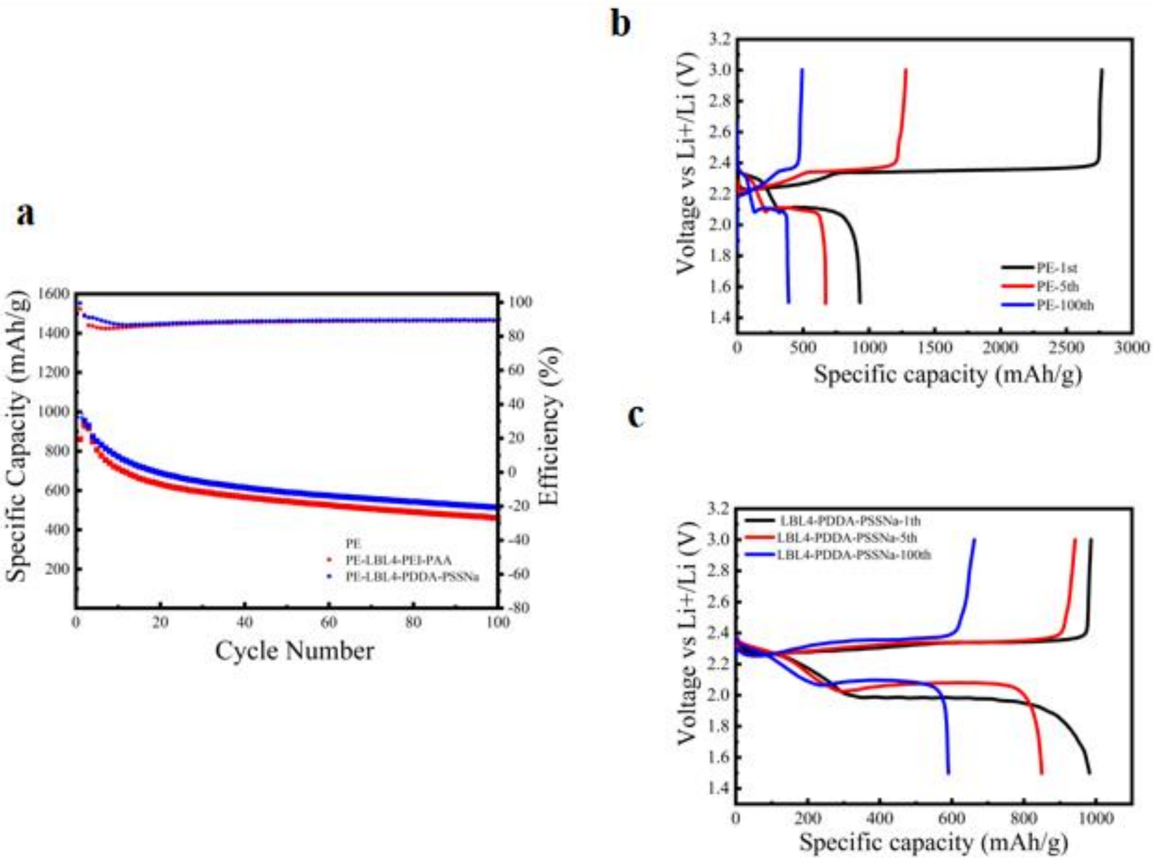


Figure 5. (a) shows the cycle performance of PE, LBL4-PEI-PAA and LBL4-PDDA-PSSNa, (b) shows the charge and discharge curve of PE, (c) shows the charge and discharge curve of LBL4-PDDA-PSSNa.

Improving the separator to inhibit the shuttling of lithium polysulfide has attracted the attention of many scientific researchers. Zhu's group used Nafion separators to effectively inhibit lithium polysulfide shuttles. The sulfonate in Nafion effectively inhibits the shuttling of lithium polysulfide through electrostatic repulsion. This approach can still improve the cycle stability of lithium-sulfur batteries without the use of lithium nitrate additive electrolytes (815 mAh/g after 100 cycles at 0.3 mAcm^{-2}) [47]. Jin's group used a glass fibre as the separator for Li-S batteries. The glass fibre can absorb lithium polysulfide deposits, thereby preventing the diffusion of lithium polysulfide, stabilizing the surface structure of the metal lithium anode, and improving the performance of the lithium sulfur battery (617 mAh/g after 100 cycles at 0.2 C)[46]. Zhu's group used the principle of microporous structure physical adsorption and chemical adsorption, using PANI/GO separators to realize polysulfide recycling and improve the cycle stability (597 mAh/g after 100 cycles at 0.5 C)[20]. Table 1 lists the applications of different functional separators in lithium-sulfur batteries and compares the ability of the different functional separators to inhibit lithium polysulfide shuttling and effectively improve the battery cycle stability. The method used in this article is environmentally friendly, and the preparation process is simple. This approach can still effectively inhibit the shuttling of lithium polysulfide without the use of lithium nitrate electrolyte. Compared with other batteries without lithium nitrate, this battery has better cycle stability and better Coulombic efficiency.

Table 1. This work is compared with other functional separators in lithium-sulfur batteries.

Modified separators	Cyclic stability	Lithium nitrate-containing electrolyte	Reference
PDDA-PSSNa	872.8 mAh/g at 0.2 C (100 cycles)	no	The recent work
PEO/PAA	728 mAh/g at 0.5 C (100 cycles)	yes	[16]
PANI/GO	597 mAh/g at 0.5 C (100 cycles)	yes	[20]
PANiNF/MWCNT	709 mAh/g at 0.2 C (100 cycles)	yes	[42]
Graphene oxide	708 mAh/g at 0.1 C (100 cycles)	yes	[43]
MCNT@PEG	490 mAh/g at 0.2 C (500 cycles)	yes	[44]
Glass fibre	617 mAh/g at 0.2 C (100 cycles)	yes	[45]
Lithiated Nafion	815 mAh/g at 0.3 $mAcm^{-2}$ (100 cycles)	no	[46]
PAH/PAA	400 mAh/g at 0.05 C (50 cycles)	no	[47]

4. CONCLUSION

In summary, this study utilizes a polyelectrolyte self-assembled modified ceramic separator to inhibit the shuttle effect of lithium polysulfide intermediates. First, a polyethylene (PE) separator is coated with a layer of SiO_2 to obtain a ceramic thin separator, and then, the thin ceramic separator is modified by in situ growth on it using polyelectrolyte self-assembly (LBL) technology. Compared with ordinary PE separators, modified polyelectrolyte ceramic separators have improved mechanical properties, thermal stability, and hydrophilicity on their surface and effectively inhibit lithium polysulfide shuttling. In particular, the LBL4-PDDA-PSSNa separator exhibits improved specific capacity and cycle performance, and there is no obvious overcharge. The initial specific capacity is 981.8 mAh/g. The capacity retention rate is 88.9% after 100 cycles. In addition to being applied to Li-S batteries, the method can be applied to other types of rechargeable batteries.

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