Highly porous polyacrylonitrile/graphene oxide membrane separator exhibiting excellent anti-self-discharge feature for high-performance lithium-sulfur batteries

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Abstract

Lithium-sulfur (Li-S) batteries have been considered as a promising candidate for next-generation energy-storage devices due to their high theoretical capacity and energy density. However, the severe self-discharge behavior of Li-S batteries strongly limits their use in practical applications. Here, we report a sustainable and highly porous polyacrylonitrile/graphene oxide (PAN/GO) nanofiber membrane separator that simultaneously enables large capacity and excellent anti-self-discharge capability for lithium-sulfur batteries. A low retention loss (5%) can be achieved even after a resting time of 24 h. Besides benefitting from the highly porous structure and excellent electrolyte wettability of the nanofiber separator, the improved performance can also be ascribed to the excellent barrier effects caused by the relatively high energy binding between $\text{-C}\equiv\text{N}$ and Li_2S /polysulfides and the electrostatic interactions between GO and negatively charged species (S_n^{2-}). It is, therefore, demonstrated that this GO incorporated PAN nanofiber separator with highly porous structure and excellent electrolyte wettability is a promising separator candidate for high-performance Li-S batteries.

Keywords: Graphene oxide; Polyacrylonitrile; Nanofiber; Separator; Lithium-sulfur batteries

1. Introduction

Sulfur (S) has recently received attention as a promising cathode material for high-specific-energy rechargeable lithium batteries because it has a high theoretical capacity of 1,675 mAh g⁻¹, which is calculated based on the complete reduction from S to lithium sulfide (Li₂S).^[1-11] Moreover, S is inexpensive and nontoxic. However, the use of Li-S batteries in practical applications is currently hindered by their short cycle life, severe self-discharge, and low Coulombic efficiency.^[12-14] All these challenges are mainly related to the dissolution of reduction intermediates, lithium polysulfides, in the electrolyte, resulting in parasitic reactions.^[15-18] Therefore, it is essential to suppress the diffusion of polysulfides in order to obtain high-performance Li-S batteries.

To address the challenges faced by Li-S batteries, efforts have been focused on the development of electrode materials via introducing conductive frameworks into the cathode, such as porous carbon, graphene, carbon nanotubes, metallic oxides, etc.^[19-28] For example, Lv *et al.*^[10] prepared integrated Ketjen Black/sulfur composite via a solution-polymerization followed by melt-diffusion approach and achieved a discharge capacity of 750 mAh g⁻¹ at 0.1C after 100 cycles. Nazar *et al.*^[20,21] used titanium oxide (Ti₄O₇, magneli phase) and manganese dioxide (MnO₂) as efficient polysulfide mediators for Li-S batteries and obtained high rechargeable capacities at practical current densities even with high sulfur loading. Li *et al.*^[26] synthesized sulfur impregnated carbon clusters for use as cathode material in Li-S batteries and achieved a stable capacity of over 700 mAh g⁻¹ after 300 cycles. Sulfur cathodes encapsulated in nitrogen-doped hollow carbon spheres and wrapped graphene were studied by Zhou and his coworkers,^[28] and it was found that sulfur/polysulfides were effectively suppressed in this 3D structure, leading to enhanced utilization of active materials. Although improved cell performance was achieved,

the methods used in preparing these composite materials generally involve complex, multi-step synthetic processes. In addition, the severe self-discharge of Li-S batteries induced by polysulfides has not been fully solved.

As a critical component in battery systems, the separator plays an important role in all batteries because its main function is to prevent electrical short circuit by separating positive and negative electrodes and transporting the ions between them.^[7, 29, 30] An ideal separator for Li-S batteries is expected to not only have a good ionic conductivity after absorbing the liquid electrolyte, but also can suppress the migration of polysulfides during cycling. Recently, a cationic selective Nafion modified membrane was used to suppress polysulfide diffusion, enhancing the electrochemical performance of Li-S cells.^[31-33] Yao *et al.* performed a thin conductive carbon coating on the polypropylene separator to prevent the migration of polysulfides.^[34] Although the cycling performance of the Li-S cells was improved in their work, the active material concentrations in those systems were relatively low (40-60 wt%) which significantly reduced the energy density of the cells. In addition, poor rate capability was observed in those systems which was probably due to the slow cell kinetics caused by the low porosity and poor wettability of the microporous polyolefin membranes. In the study of Chang *et al.*, a single-wall carbon nanotube (SWCNT)-modulated polypropylene was utilized as the separator.^[35] Although a capacity of 501 mAh g⁻¹ could be achieved at 0.2C after 300 cycles, the cell using this separator still had a relatively poor rate capability.

Nanofiber membranes are attractive for use as battery separators because they have highly porous structure and excellent electrolyte wettability, which can lead to large electrolyte intake and consequently high ionic conductivity when placed in the electrolyte, facilitating rapid ionic transportation.^[36-40] Many polymers can be used to prepare nanofiber membranes. Among

them, polyacrylonitrile (PAN) is believed to be a suitable polymer for battery separator application because of its easy processability and excellent resistance to oxidative degradation.^[41] Tatsuma *et al.* and Gopalan *et al.* found that the use of PAN separators led to reduced lithium dendrite sizes because the viscoelastic polymer could mechanically suppress dendrite formation.^[42, 43] In addition to PAN, graphene oxide (GO) has received a lot of attention recently.^[44, 45] GO membrane was also demonstrated to be able to block the diffusion of polysulfides which was ascribed to the electrostatic interactions between the negatively charged species (S_n^{2-}) and the oxygen-containing groups on GO.^[46] For example, Zeng *et al.* used electroactive cellulose-supported GO interlayers in Li-S cells, and found that the GO interlayers could minimize the diffusion of polysulfides, enhancing the utilization of active material.^[47] Zhuang *et al.* also reported that the GO sheets could act as physical barriers to suppress the diffusion of polysulfide anions, improving the electrochemical performance of Li-S batteries.^[48]

Based on the abovementioned considerations, we report an effective PAN/GO nanofiber membrane separator that can provide Li-S cells with significantly enhanced cycle stability and rate capability without introducing complicated cathode structure design. More importantly, a low capacity retention loss (5%) can be achieved even after a resting time of 24 h, indicating excellent anti-self-discharge capability of the PAN/GO nanofiber membrane. It is, therefore, demonstrated that this PAN/GO nanofiber membrane can be considered as a promising separator candidate for advanced Li-S batteries.

2. Experimental

2.1. GO synthesis

GO was synthesized based on an improved method.^[49] Briefly, 1.5 g graphite powder (< 20 micro, Sigma-Aldrich) and 9 g potassium permanganate (KMnO₄, ≥99%, Sigma-Aldrich) were added to a mixture of 180 mL sulfuric acid (H₂SO₄, 95-98%, Sigma-Aldrich) and 20 mL phosphoric acid (H₃PO₄, ≥85%, Sigma-Aldrich). The mixture was then heated to 50 °C followed by mechanical stirring for 12 h. After that, the mixture was cooled to room temperature and poured onto the ice (180 g) with a certain amount of 30 wt% hydrogen peroxide (H₂O₂, 30 wt%, Sigma-Aldrich). The solution color changed from dark green to bright yellow. The solution was then centrifuged at 3500 rpm for 30 min. The obtained material was washed by 100 mL of deionized (DI) water, 100 mL of 37 wt% hydrochloric acid (HCl, Sigma-Aldrich), and 200 mL of ethanol (EtOH, 99.5%, Sigma-Aldrich). The time for each wash was 15 min. Finally, the as-prepared GO was vacuum-dried at 60 °C for 6 h.

2.2. Membrane preparation

A homogenous solution of 3 g polyacrylonitrile (PAN, *M_w* = 150, 000, Sigma-Aldrich) in 27 g dimethylformamide (DMF, >99.5%, Sigma-Aldrich) was prepared and then electrospun to form a PAN nanofiber membrane under a high voltage of 15 kV with a feeding rate of 0.75 mL min⁻¹.^[50, 51] For the preparation of PAN/GO nanofiber membrane, 0.3 g GO was firstly dispersed into DMF with the assistance of sonication. Then, 3 g PAN was added into the GO dispersed solution. The weight ratio between PAN and GO in the as-spun PAN/GO nanofiber membrane was 10:1, corresponding to a GO content of 9.1 wt%. The average thicknesses of these as-spun membranes were in the range of 65 ± 3 μm. Polypropylene (PP, Celgard 2400) membrane was used for comparison in this study.

2.3. Structure characterization

The size and thickness of GO were evaluated by using atomic force microscopy (AFM, Bruker Dimension 3000, USA). Field-emission scanning electron microscopy (FE-SEM, FEI Verios 460L, USA) was performed to observe the morphology of PAN and PAN/GO nanofiber membranes. X-ray diffraction (XRD, PANalytical Empyrean, Holland) was used to identify the structure of the as-prepared nanofibers. The surface functional groups of PAN and PAN/GO nanofiber membranes were characterized by using X-ray photoelectron spectroscopy (XPS, SPECS FlexMod, Germany) with Mg K α X-ray source.

The porosities of the as-prepared membranes were measured by using n-butyl alcohol (99%, Sigma-Aldrich) uptake test and calculated by:

$$Porosity (\%) = (w_w - w_d) / (\rho_b \times V) \times 100\% \quad (1)$$

where w_w and w_d are the weights of wet and dry separators, ρ_b stands for n-butyl alcohol's density, and V is the geometric volume of the separator.

The electrolyte uptakes (EU) were determined by soaking weighed separators in the liquid electrolyte of 1 M lithium bis(trifluoromethane)sulfonamide lithium (LiTFSI, Sigma-Aldrich) and 0.1 M lithium nitrite (LiNO₃, 99.99% trace metals basis, Sigma-Aldrich) in a mixture of 1,3-dioxolane (DOL, Sigma-Aldrich) and 1,2-dimethoxyethane (DME, Sigma-Aldrich) (1: 1 by volume) at room temperature for 2 h. The EU values were calculated by:

$$EU (\%) = (w_I - w_0) / w_0 \times 100\% \quad (2)$$

where w_0 and w_I are the weights of separators before and after soaking in the electrolyte, respectively.

The ionic conductivities (σ) of electrolyte-soaked separators were determined based on the electrochemical impedance spectroscopy (EIS) test. The measurements were carried out after the separators fully adsorbed the liquid electrolyte and reached the equilibrium. The σ values were calculated by:

$$\sigma = L / (R_b \times A) \quad (3)$$

where R_b is the electrolyte's bulk resistance, L and A are the thickness of the separator and the contact area between the stainless steel electrode and the separator, respectively, which are 65 μm and 1.89 cm^2 .

2.4. Electrochemical performance evaluation

Coin-type 2032 Li-S cells were assembled in an argon-filled glove box to evaluate the electrochemical performance of PAN and PAN/GO nanofiber separators. The cathode was prepared by mixing 70 wt% sulfur (99.5-100.5%, Sigma-Aldrich) and 20 wt% Super P (C-65, TIMCAL Graphite & Carbon Ltd.) with 10 wt% polyvinylidene fluoride (Solef[®]PVDF-5130, Solvay) and certain amount of N-methyl-2-pyrrolidone (NMP, 99%, Sigma-Aldrich) to form a slurry which was then coated on the carbon coated aluminum foil and dried under vacuum at 60 °C for 12 h. Lithium metal foil was used as the anode and 1 M LiTFSI with 0.1 M LiNO₃ in a mixture of DOL/DME (1: 1 by volume) was used as the electrolyte. The sulfur loading was around 0.7-1 mg cm^{-2} and the amount of electrolyte in different coin cells was fixed at 40 μL per 1 mg S. The polysulfide solution with 0.02 M Li₂S₈ was used for the polysulfide diffusion test. The cycling performance of assembled Li-S cells was evaluated by using Arbin Instruments in a potential range of 2.8-1.7 V. The specific capacities of the cells used in this study were calculated based on the sulfur mass in the cathode.

The cyclic voltammetry (CV) measurement was conducted using a Gamry Reference 600 with different scanning rates in a potential range of 2.8-1.7 V. Lithium-ion diffusion coefficient D_{Li^+} ($\text{cm}^2 \text{s}^{-1}$) was measured by CV with different scanning rates and calculated according to the Randles-Sevick equation:

$$I_p = 2.69 \times 10^5 n^{1.5} A D_{\text{Li}^+}^{0.5} C_{\text{Li}^+} \nu^{0.5} \quad (4)$$

where I_p is the peak current in A, n is the number of electrons in the reaction (it is 2 for Li-S battery), A is the electrode area in cm^2 , C_{Li^+} and ν represent the lithium-ion concentration in the electrolyte in mol mL^{-1} and the CV scanning rate in V s^{-1} , respectively.

3. Results and discussion

3.1. Morphology and structure characterization

The purpose of this work is to obtain PAN/GO nanofiber separator that is able to minimize the polysulfide diffusion in Li-S batteries. While suppressing the polysulfide diffusion, the PAN/GO nanofiber separator should also have the structure features of high porosity and good electrolyte wettability so that the lithium cations can transport freely between the two electrodes. The scanning electron microscopy (SEM) image of PAN/GO nanofiber separator is shown in Figure 1. For comparison, the SEM images of microporous PP membrane separator and PAN nanofiber separator are also shown. Unlike slit-like porous structure of polypropylene (PP) (Figure 1a), both PAN and PAN/GO nanofiber separators consist of randomly arranged fibers with average diameters of 850 and 600 nm, respectively. The high-resolution SEM images in Figure 1 present that the PAN/GO nanofiber has a relative rough surface, which might indicate the aggregation of GO. The randomly arranged fibers assemble to form a network structure with

open pores in the macroscale range. This highly porous structure is further confirmed by the porosity testing results, as shown in Table 1. The porosities of PAN and PAN/GO nanofiber separators are 70% and 72%, respectively, which are significantly higher than that (41%) of PP separator. It should be noted that the use of high-porosity PAN and PAN/GO membranes might increase the risk of short circuit for Li-S cells. Min *et al.*^[41] used a PAN membrane (porosity = 68%) as Li-ion battery separator and found that the open pores in the membrane disappeared after the uptake of liquid electrolyte, which was caused by the gelation of PAN in liquid electrolyte. This indicated that PAN based separators might reduce the short circuit risk for Li-S batteries. However, efforts are still needed to permanently eliminate the short circuit behavior. One possible approach is to coat the lithium anode with a mechanically-strong, ionically-conductive non-porous layer. Another concern for the use of high-porosity PAN and PAN/GO separators is that Li dendrites might pass through them easily when Li anode is used. However, Tatsuma *et al.*^[42] found that the use of PAN membrane reduced the size of lithium dendrites because the viscoelastic polymer mechanically suppresses dendrite growth. Similar phenomenon has been discovered by Gopalan *et al.*^[43] Although PAN-based membranes could potentially inhibit the lithium dendrite growth, this is not a permanent solution. Therefore, other approaches must be studied to avoid the lithium dendrite growth, and the abovementioned non-porous coating layer on lithium anode could be an effect solution to solve the dendrite problem.

Figure 2 shows the X-ray diffraction (XRD) patterns of pure PAN and PAN/GO nanofiber separators. The XRD spectrum of PAN nanofiber separator displays a sharp intense peak at 16.7° and a weak diffraction peak at 28.5°. The first peak is corresponding to the (100) diffraction of the hexagonal lattice and the second peak is ascribed to the second-order diffraction of the first peak.^[52] After the introduction of GO filler, the XRD pattern of PAN/GO

nanofiber separator shows an additional peak at 10.5° , corresponding to the (002) reflection of GO (Figure S1, Supporting Information), while still presenting the PAN peaks at 16.7° and 28.5° . The appearance of both PAN and GO peaks indicates that the electrospinning method did not change the structure of GO filler and PAN chains. It is important to note that the size and thickness of the GO used in this work are around 500 nm and 1.332 nm, respectively (Figure S2).

XPS was applied to identify the surface functionality of as-spun PAN and PAN/GO nanofiber separators (Figure 3). The peaks at 398 and 284 eV for both PAN and PAN/GO membranes are corresponding to N1s and C1s of the $-\text{C}\equiv\text{N}$ groups as well as the main chain of polyacrylonitrile. A small oxygen peak can be detected in PAN/GO nanofiber separator (Figure 3b) due to the presence of oxygen-containing functional groups (such as ketone carbonyls, ester and lactol carbonyls, etc.) in GO.^[49] The relatively low intensity of oxygen is ascribed to the low concentration of oxygen in the PAN/GO nanofiber separator. As expected, there is no oxygen detected for the PAN membrane (Figure 3a).

The unique structural features of PAN/GO nanofiber separator can play an important role in improving the overall performance of Li-S cells. As shown schematically in Figure 4, when PAN/GO nanofiber separator is used, the lithium cations can transport freely across this high porous network structure, which guarantees the high capacity and excellent rate capability of the Li-S cells. At the same time, the anions of polysulfides are confined on the cathode side and the shuttle of polysulfides between the cathode and anode sides can be significantly minimized due to the relatively high energy binding between the $-\text{C}\equiv\text{N}$ groups of PAN and the Li_2S /polysulfides in the electrolyte and the electrostatic interactions between the oxygen-containing functional groups of GO and the negatively charged species (S_n^{2-}) of polysulfides. As a result, this highly porous PAN/GO membrane can not only block the diffusion of polysulfides

but also improve the ionic conductivity which are beneficial for improving the cycling performance, rate capability and anti-self-discharge capability of Li-S cells. The electrochemical performance of Li-S cells using PAN/GO nanofiber separator was characterized and discussed below.

3.2. CV and discharge-charge profiles

CV tests were conducted to investigate the electrochemical behavior of the Li-S cells at a scan rate of 0.1 mV s^{-1} . As shown in Figure 5a, the CV curve of the cell with PP separator exhibits two cathodic peaks at around 2.21 and 1.96 V and two overlapped anodic peaks at around 2.41 and 2.47 V, which are typical of Li-S cells. Similar results have also been found for the Li-S cells with PAN (Figure 5b) and PAN/GO (Figure 5c) separators.

The discharge-charge profiles of the first cycle for Li-S cells with PP, PAN, and PAN/GO separators at 0.2C are shown in Figure 6. The C rates specified in this study are based on the mass and theoretical capacity of sulfur ($1 \text{ C} = 1,675 \text{ mA g}^{-1}$). In general, there are two discharge regions based on the voltage profile in the reduction process of Li-S battery, which are in the range of 2.4-2.1 V (the first region) and 2.1-1.7 V (the second region), respectively. The first region represents the formation of long-chain polysulfides (Li_2S_n , $4 \leq n \leq 8$) by the reduction of elemental sulfur and the second discharge region indicates the conversion of Li_2S_4 to solid-phase low-order Li_2S_2 or Li_2S . During the cell charging, the two continuous charge plateaus correspond to the oxidation reactions from lithium sulfides to polysulfides and finally to sulfur. From Figures 6a and b, it is seen that both the charge and discharge capacities of the Li-S cell with PAN separator is slightly higher than those with PP separator, which is due to the relatively higher binding energy between the $-\text{C}\equiv\text{N}$ and Li_2S /polysulfides compared with that between $-\text{CH}_3$ and Li_2S /polysulfides, suppressing the diffusion rate of polysulfides and

improving the active material utilization. The binding energies between $-\text{C}\equiv\text{N}$ and Li_2S /polysulfides are 0.60 eV and 0.77 eV, while the binding energies between $-\text{CH}_3$ and Li_2S /polysulfides are 0.23 eV and 0.30 eV, respectively.^[53] As shown in Figure 6c, the Li-S cell with PAN/GO separator has the highest charge and discharge capacities among all three cells. This is probably because the electrostatic interactions between GO and negatively charged species (S_n^{2-}) help minimize the migration of polysulfide intermediates and further enhance the utilization of active material.^[46]

3.3. Cycling and rate performance

Cycling performance of Li-S cells with PP, PAN, and PAN/GO separators was tested at a current density of 0.2C, and the results are shown in Figure 7. The initial discharge capacity for Li-S cells with PP, PAN, and PAN/GO separators are 781, 868, and 987 mAh g^{-1} , respectively. As discussed above, the higher discharge capacity of the Li-S cell with PAN separator than that with PP separator is caused by the relatively higher binding energies between the $-\text{C}\equiv\text{N}$ and Li_2S /polysulfides compared with those between $-\text{CH}_3$ and Li_2S /polysulfides, suppressing the diffusion rate of polysulfides and improving the active material utilization.^[44] The Li-S cell with PAN/GO separator has the highest discharge capacity among the three cells because the strong electrostatic interactions between GO and negatively charged species (S_n^{2-}) further minimize the migration of polysulfide intermediates and enhance the utilization of active material.^[46, 48] After 100 cycles, the cell with PAN/GO separator can still deliver a high capacity of 597 mAh g^{-1} which is 38% higher than that of the cell with PP separator. Such improved cycling performance is due to the relatively high energy binding between $-\text{C}\equiv\text{N}$ and Li_2S /polysulfides and the electrostatic interactions between GO and negatively charged species (S_n^{2-}), effectively blocking the polysulfides transportation and further enhancing the utilization of the active material.

Since the rate capability is considered as another essential parameter for batteries, the Li-S cells were also tested under various current densities from 0.2 to 2C rate. As seen in Figure 8, the cell with PP separator can deliver specific capacities of 445, 382, and 303 mAh g⁻¹ at current densities of 0.2, 0.5, and 1C, respectively. When the current density increases to 2C, the capacity drops rapidly to 129 mAh g⁻¹. For comparison, the cell with PAN separator shows relatively stabilized and higher capacities of 580, 485, and 391 mAh g⁻¹, respectively, at current densities of 0.2, 0.5, and 1C. A capacity of 257 mAh g⁻¹ can be obtained at the current density of 2C for the Li-S cell with PAN separator. The improved electrochemical performance is probably due to the formation of LiS_n···N interactions via the N lone-pair electrons, which alleviates the dissolution of lithium polysulfides in the electrolyte and enhances the active material utilization.^[54] For the cell with PAN/GO separator, the capacity gradually decreases from 699 to 591, 448 mAh g⁻¹, respectively, when the current density increases from 0.2 to 0.5, 1C. At a high current density of 2C, the capacity (337 mAh g⁻¹) achieved by the cell with PAN/GO separator is significantly higher than those (129 and 257 mAh g⁻¹) of the cells with PP and PAN separators. More importantly, when the current density is switched back from 2C to 0.2C, the Li-S cell with PAN/GO separator can still deliver a reversible capacity of 655 mAh g⁻¹ (a high retention of 94%), which is 80% and 25% higher than those (364 and 525 mAh g⁻¹) of the cells with PP and PAN separators. The excellent rate capacity of the Li-S cell with PAN/GO separator can be ascribed not only to the highly porous structure of the separator, resulting in good ionic conductivity (1.36 mS cm⁻¹, as can be seen in Table 1), but also to the relatively high energy binding between -C≡N and Li₂S/polysulfides and the electrostatic interactions between GO and negatively charged species (S_n²⁻), availably suppressing the diffusion of polysulfides.

3.4. Lithium-ion diffusion coefficients

It is necessary to investigate the impact of GO on lithium-ion diffusion since the rate performance is closely associated with the diffusion of lithium ions in the cells. The lithium-ion diffusion coefficients were evaluated by a series of cyclic voltammetry (CV) measurements with different scan rates (shown in Figures 9a-c) and calculated by the Randles-Sevcik equation.^[55, 56] Here, the cathodic peaks at ~2.2 V and ~1.95 V and the anodic peak at ~2.45 V were defined as peaks A, B, and C, respectively. According to Equation (4), the plot of the reduction peak current I_p versus the square root of the scan rate should result in a straight line which is confirmed by Figures 9d-f. From the slope of the linear fit, the lithium diffusion coefficients are calculated to be $D_{Li^+}(A) = 2.90 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $D_{Li^+}(B) = 6.36 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, and $D_{Li^+}(C) = 1.07 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for the Li-S cell with PP separator. The diffusion coefficients increase to $D_{Li^+}(A) = 5.51 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $D_{Li^+}(B) = 6.71 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $D_{Li^+}(C) = 1.55 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ when PAN separator was used. After the addition of GO in PAN, the diffusion coefficients further increase to $D_{Li^+}(A) = 8.25 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $D_{Li^+}(B) = 1.15 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, and $D_{Li^+}(C) = 2.34 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. It is obvious that the lithium ion diffusion coefficients can be dramatically enhanced when using PAN and PAN/GO separators, which is attributed to their highly porous structure and excellent electrolyte uptake ability. As shown in Table 1, the electrolyte uptake of the PAN and PAN/GO separators are 275% and 303%, respectively, which are significantly higher than that (152%) of the PP separator.

3.5. Anti-self-discharge capability

It should be noted that low self-discharge is another important requirement for determining the practicality of Li-S batteries. Unfortunately, conventional Li-S batteries exhibit severe self-discharge behavior. The evolution of open-circuit voltages (OCV) with time for Li-S cells using PP, PAN and PAN/GO separators are shown in Figure S3. It is seen that the OCV

value of the cell with PP separator dropped from 2.44 V to 2.39 V after 10 h of storage, while the OCV of the cell with PAN separator kept a stable value of 2.40 V even after 120 h. For the cell with PAN/GO separator, the OCV is stabilized at a high value of 2.73 V, demonstrating its excellent anti-self-discharge behavior. Since the self-discharge of Li-S batteries is largely caused by the continuous dissolving of sulfur/high-order polysulfides in the electrolyte even in the resting state after charging due to the presence of concentration gradients, in this work, the discharge capacity after resting was also used to describe how the PAN/GO separator contributes to the anti-self-discharge feature. The capacity retention was defined as the capacity ratio between the second cycle and the first cycle. The capacity retention of the Li-S cell with PP separator is 86% without resting (Figure 10a). However, the capacity retention decreases to 51% when there is a 24 h rest between the first and second cycle (Figure 10d). This indicates that a high retention loss of 35% (86% - 51%) can be observed for the cell using PP separator if there is a 24 h rest between the first two cycles. As shown in Figures 10b and e, the retention loss after 24 h rest decreases to 28% (90% - 62%) when PAN separator is used, which is probably because of the relatively higher binding energy between the $\text{-C}\equiv\text{N}$ and Li_2S /polysulfides compared to that between -CH_3 and Li_2S /polysulfides.^[53] After the introduction of GO into PAN, a significantly lower retention loss of 5% (79% - 74%) can be obtained for the cell using PAN/GO separator, indicating the excellent anti-self-discharge behavior (Figures 10c and f). Besides benefitting from the binding ability of the $\text{-C}\equiv\text{N}$ groups in PAN, the oxygen-containing electronegative groups in GO act as ion-hopping sites of Li^+ and minimize the transportation of negatively charged species (S_n^{2-}) through the formation of electrostatic interactions, which in turn enhances the anti-self-discharge capability of Li-S cells.

In addition, as shown in Figure S4, the diffusion of polysulfides through PP, PAN and PAN/GO separators was observed by using a diffusion model. It is clear that polysulfides were totally blocked by all three separators at the beginning. After 30 min, the color of the electrolyte with PP separator turned to yellow. However, there was no color change when PAN and PAN/GO separators were used, indicating their excellent ability of suppressing the polysulfide diffusion.

4. Conclusions

In summary, PAN/GO nanofiber separator was prepared for Li-S batteries to enhance the cycle stability and rate capacity even with high sulfur content of 70 wt% in the cathode. The improved performance is attributed to a variety of synergic effects, including highly porous structure and good wettability of PAN/GO nanofibers, as well as the physical and chemical barrier effects of PAN chains, which have $\text{--C}\equiv\text{N}$, and GO filler, which contains various oxygen-containing functional groups. The Li-S cell made with PAN/GO separator is able to demonstrate high specific capacity, excellent rate capability, and enhanced anti-self-discharge capability. More importantly, this work offers a general strategy to apply GO-based polymer membrane for use as novel separator to achieve high-performance Li-S batteries, enhancing their commercial viability.

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Table and Figure Captions

Table 1. Physical and electrochemical parameters of PP, PAN, and PAN/GO separators.

Figure 1. SEM images of (a) PP, (b) PAN, and (c) PAN/GO separators, the inserts are high resolution images.

Figure 2. XRD patterns of PAN and PAN/GO separators.

Figure 3. XPS survey spectra of (a) PAN and (b) PAN/GO separators.

Figure 4. Schematic illustration of the Li-S cell with PAN/GO separator.

Figure 5. CV curves of Li-S cells with (a) PP, (b) PAN, and (c) PAN/GO separators at a scan rate of 0.1 mV s^{-1} .

Figure 6. The first discharge-charge profiles of Li-S cells with (a) PP, (b) PAN, and (c) PAN/GO separators.

Figure 7. Cycling performance of Li-S cells with PP, PAN, and PAN/GO separators at a current density of 0.2C .

Figure 8. Rate performance of Li-S cells with PP, PAN, and PAN/GO separators under varying current densities.

Figure 9. CV curves at various voltage scan rates of Li-S cells with (a) PP, (b) PAN, and (c) PAN/GO PP separators; the linear fits of the peak currents for Li-S cells with (d) PP, (e) PAN, and (f) PAN/GO separators.

Figure 10. Discharge-charge profiles and self-discharge behavior of Li-S cells with (a, d) PP, (b, e) PAN, and (c, f) PAN/GO separators at a current density of 0.2C .

Table 1. Physical and electrochemical parameters of PP, PAN, and PAN/GO separators.

Sample	Porosity (%)	Electrolyte Uptake (%)	Ionic Conductivity (mS cm ⁻¹)
PP	41	152	0.60
PAN	70	275	1.00
PAN/GO	72	303	1.36

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