Electrospun graphene oxide (GO)/polyvinylidene flfluoride (PVDF) nanofiber separator for lithium-ion battery

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In order to develop a high-performance separator for lithium-ion battery, in this paper, GO/PVDF composite fiber membrane with different GO content was prepared by electrospinning, and the lithium-ion batteries were assembled by using it as the separator, and the performance of the battery was tested. The spinning results show that the high content of GO may affect the normal process of electrospinning, and the average diameter of fibers in GO/PVDF film increases with the increase of the quality of GO. The battery performance test results show that the performance of the battery assembled by GO/PVDF fiber membrane is better than that of PVDF fiber membrane, the addition of GO significantly improves the cycle performance of the battery, and GO/PVDF fiber membrane is more suitable for lithium-ion battery than PVDF fiber membrane.

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Keywords: GO, PVDF, Electrospinning, Separator, Lithium-ion battery

1. Introduction

As a new generation of batteries, lithium-ion batteries have many excellent performances, such as no memory effect, high specific energy, long service life, many charge and discharge cycles, green pollution, no pollution and higher safety performance [1-3]. Therefore, in today's energy shortage and environmental degradation, research and development of high-performance lithium-ion batteries is of great significance.

One of the bottlenecks in the development of lithium-ion batteries is the diaphragm material. The lithium-ion battery separator is a porous membrane material placed between the positive electrode and the negative electrode of the battery [4,5], and its function is to prevent direct contact between the positive and negative active materials and prevent internal short circuit of the battery [6-8]. The structure and the internal resistance of the battery are determined by the performance of the diaphragm. At the same time, the comprehensive performance of the lithium-ion battery is closely related to the performance of the separator [9,10]. At present, the commercial lithium-ion battery separator has the defect of poor affinity with the electrolyte, so that the electrolyte can not swell well with the diaphragm, and the electrolyte is prone to side leakage, which makes the safety of the lithium-ion battery have hidden dangers [11,12]. Therefore, there is an urgent need to develop a high performance and low cost lithium ion battery separator.

Electrospinning is an efficient technology for producing nanofibers membranes with small pore size, high porosity, and high liquid absorption rate [13-15]. It is an ideal battery membrane material. Therefore, many researchers focus on the preparation of lithium-ion battery membrane by electrospinning. At present, there are many electrospinning polymer systems [16] for the preparation of lithium-ion battery membrane, such as polyvinylidene flfluoride (PVDF), polyacrylonitrile (PAN), polymethyl methacrylate (PMMA), Polyethylene oxide (PEO), etc. PVDF possesses numerous C–F chemical bonds, leading to good chemical stability, high dielectric constant, and low surface energy. Hence, it received increasing attention as a promising host for electrolyte in LIBs [17]. However, due to the regular structure and high crystallinity of PVDF, the ionic conductivity of PVDF is low. Recent studies have shown that adding inorganic fillers such as SiO_2 [18, 19], TiO_2 [20]and Al_2O_3 [21] to electrospinning solution to prepare composite nanofiber membrane is an effective method to improve the performance of lithium-ion battery diaphragm.

Graphene oxide (GO) has good hydrophilicity, high specific surface energy and mechanical properties. GO has been demonstrated to be effective in producing perm-selective membranes for lithium batteries given the negative charge that facilitates Li ion permeability and

hinders anion crossover by electrostatic repulsion and steric hindrance [22].

In this paper, GO was added into PVDF solution, and GO/PVDF composite fiber membrane was prepared by electrospinning. The spinnability of GO/PVDF was studied. Then the lithium-ion battery was assembled with GO/PVDF as the membrane to study the performance of the battery.

2. Experimental

2.1. Materials

Polyvinylidene fluoride (PVDF), high purity single layer graphene oxide (GO), DMF (Analytica purity), Acetone (Analytical purity), Diaphragm of GO/PVDF composite fiber membrane, Anode material: Lithium cobaltate, Cathode material: lithium sheet, Electrolyte: LIB315, electrolyte LiPF6 (1mol/L), Solvent volume ratio EC: EMC: DMC = 1:1:1, The positive active mass is 29.6mg, Gasket, elastic piece.

2.2. Instruments

Electrospinning machine, S-4800-I Field emission scanning electron microscope, Electric Universal Testing Machine, Differential Scanning Calorimeter (model: 214Polyma, NETZSCH Scientific Instruments Trading (Shanghai) Ltd.), Blue battery test system (model: CT2001A, Wuhan Landian Electronics Co., Ltd), Glove box (model: Eteluxlab2000 Itex Inert Gas System Co., Ltd)

2.3. Preparation of GO/PVDF Composite Nanofibers

A certain amount of PVDF powder was added to the DMF/ Acetone solution (PVDF concentration is 12 wt.% and mass ratios of DMF to Acetone is 8:2, then Go powder were added to the solution. This solution was sealed and stirred 4h to prepare spinning solution. Then, spinning solution was made into GO/PVDF composite nanofibers by electrospinning device. The parameters of electrospinning were set up as follows: the voltage was 15kv, distance between the needle tip and the collector was 20cm and flow rate was 0.8mL/h. The mass fraction of GO in GO/PVDF composite nanofibers are respectively 0wt%, 0.5wt%, 1wt%, 1.5wt% and 2wt%.

2.4. Lithium-ion batteries assembly

Firstly, the fiber membrane is cut into small discs with a diameter of about 20 mm, and the thickness is about 30 um, as shown in Fig. 1. Then, in a glove box filled with argon gas, the anode, the diaphragm, the cathode, the gasket, and the elastic piece are sequentially placed in the anode and cathode shells in the order of Fig. 2, drip an appropriate amount of electrolyte, Finally, the button battery is compacted and assembled into a button battery CR2032, which is 20mm in diameter and 3.2mm in thickness (Fig. 3). It is allowed to stand for more than 24 hours.

2.5. Characterization

Morphology of GO/PVDF composite nanofibers was observed by SEM. Also, in each SEM image, 50 fibers were chosen randomly to be measured by Photoshop, and then mean fiber diameter and standard deviation were calculated. The crystallinity of GO/PVDF fiber membrane is measured by DSC. The breaking strength of GO/PVDF membrane is measured by Electric Universal Testing Machine. With a constant current rate 0.2 C and the charge-discharge voltage range 2.8-4.2 V, 50 charge-discharge cycles are tested, then the first charge discharge curve and cycle stability of the lithium-ion battery are obtained.

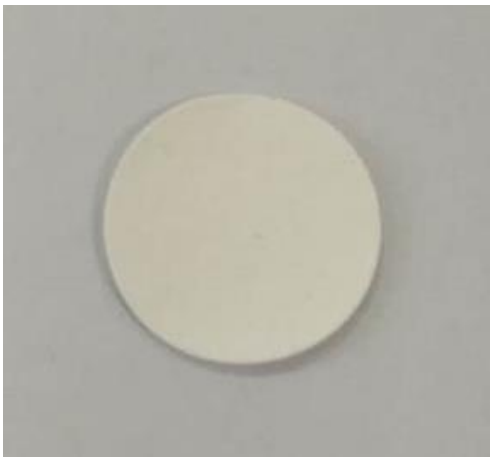


Fig.1. Diaphragm (color online)

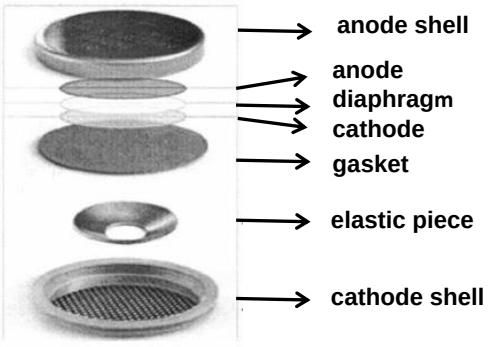


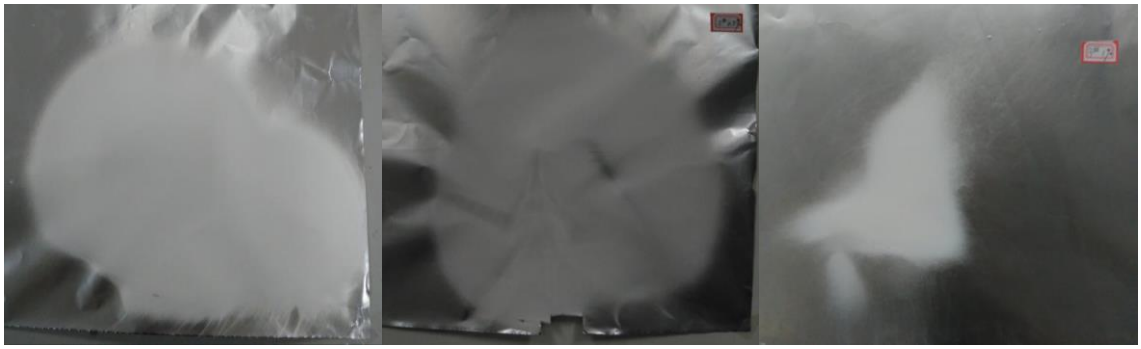
Fig. 2. Assembly sequence

Fig. 3. Button battery CR2032 (color online)

3. Results and discussions

3.1. Electrospun GO/PVDF fiber membrane

GO/PVDF nanofiber membrane is shown in Fig. 4. When the mass fraction of GO is 2wt%, there is a phenomenon that fibers cannot be collected by a large number of receiving plates in the spinning process. The fibers are deposited on the insulating plate in front of the injection pump, or suspended between the insulating plate and the receiving plate, or fall on the insulating plate at the bottom, and cannot be sprayed on the receiving aluminum plate to form a large fiber film. This may be because the amount of GO added is too large to affect PVDF fiber formation.



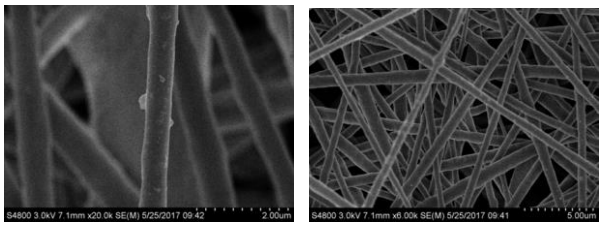
(a) *(b)* *(c)*

(d) *(e)*

Fig. 4. GO/PVDF fiber membrane. The mass fractions of GO in (a), (b), (c), (d), (e) are: 0 wt%, 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%, respectively (color online)

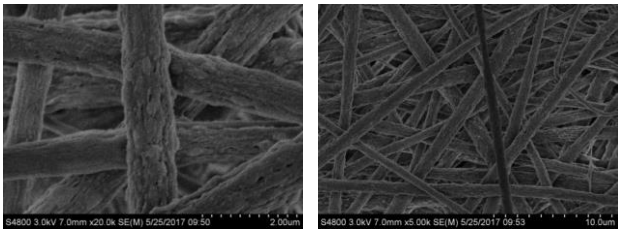
The micro structure of GO/PVDF fiber is observed as Fig. 5. It is found that the surface of the fiber without adding GO is basically smooth and occasionally has raised defects.

After adding graphene oxide, the surface of the fiber becomes very rough and seems to have holes, and there are many raised particles on the surface, so it is speculated that it is nanoparticles of GO.



Magnification 20000 times Magnification 6000 times

(a)



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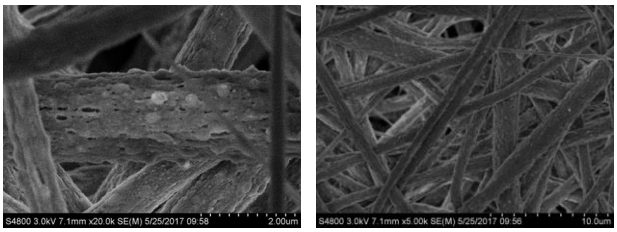
(b)



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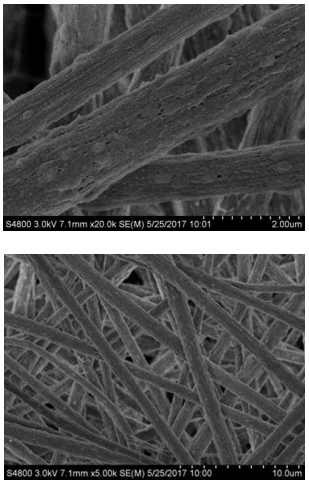
(c)



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(d)

Fig. 5. SEM image of GO/PVDF electrospun fiber membrane. The mass fractions of GO in (a), (b), (c), and (d) were: 0 wt%, 0.5 wt%, 1 wt%, and 1.5 wt%, respectively

The Photoshop software was used to measure the diameter of the first four experimental fibers, and the average diameter and diameter standard deviation were calculated in Table 1. According to the calculated data of Table 1, the GO/PVDF fiber average diameter line graph and the GO/PVDF fiber diameter standard deviation line graph were drawn (Fig. 6, Fig. 7). Fig. 6 and Fig. 7 show as the GO concentration increases, the average fiber diameter gradually increases, and the standard deviation of the fiber diameter first increases and then decreases.

Table 1. Diameter of composite nanofibers

The mass fraction of GO(wt%)	Mean fiber diameter (nm)	Standard deviation (nm)
0	616	206.11
0.5	954	188.63
1.0	1062	421.09
1.5	1149	217.45

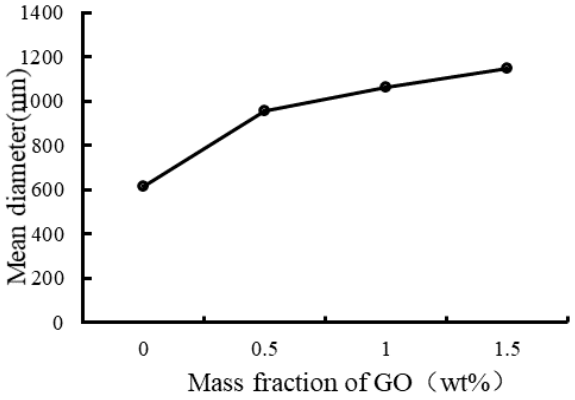

Fig. 6. GO/PVDF fiber average diameter line chart

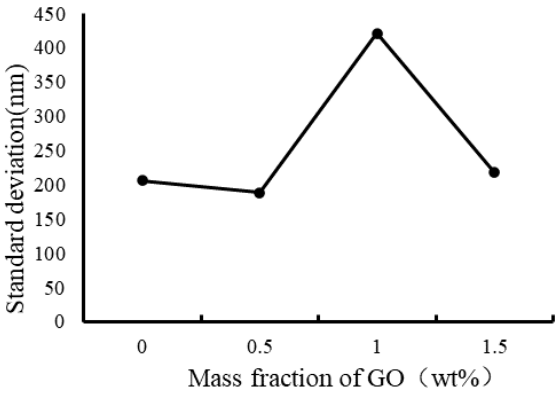

Fig. 7. GO/PVDF fiber diameter standard deviation line chart

The crystallinity of GO/PVDF fiber membrane is calculated in Table 2. The higher the crystallinity, the worse the kinematic performance of the molecular chain, which makes it difficult to transport ions, so the lower the ionic conductivity. The crystallinity of fiber membrane containing GO is less than that of fiber membrane without GO, which shows that the addition of GO can reduce the crystallinity of PVDF. The crystallinity of the fiber membrane is the lowest when the

GO content is 0.5%. With the increase of GO content, the crystallinity of fiber membrane increases, which implies that the amount of go added is not the greater the better.

Table 2. Crystallinity of composite nanofibers

The mass fraction of GO(wt%)	Crystallinity(%)
0	65.41
0.5	51.18
1.0	53.66
1.5	54.43

The breaking strength of GO/PVDF fiber membrane is calculated in Table 3. It can be seen that after adding GO, the breaking strength of fiber membrane decreases, and the strength of fiber membrane decreases with the increase of GO content. This is because after GO is added, the particles adhere to the macromolecular chain, which makes the crystalline region of the polymer unstable, the amorphous region increases, the macromolecular activity increases, and the fiber is easier to deform after friction and tension.

Table 3. Breaking strength of composite nanofibers

The mass fraction of GO (wt%)	Breaking Strength (cN)
0	238
0.5	176
1.0	145
1.5	86

Combined with the observation of fiber morphology and the calculation of fiber average diameter and diameter uniformity, the following conclusions were made.

(1) When the GO was added, the macroscopic morphology of the fiber membrane did not change, but when the magnification is 20,000 times, the microscopic morphology of the fiber was found to vary greatly. The roughness of the fiber surface is obviously increased, the appearance is uneven, there are voids, and there are also grain protrusions, and the fibers are no longer smooth and straight.

(2) As the quality of the added GO increases, the average diameter of the fibers in the PVDF film also increases. The addition of GO also deteriorates the diameter uniformity of the fibers and broadens the diameter distribution. The addition of GO reduced the crystallinity of the fiber membrane.

(3) The amount of GO added should be appropriate, and excessively large may affect the normal filament formation of the electrospun fiber and breaking strength of the fiber membrane.

In summary, the amount of GO added in this experiment is preferably 0.5% by weight.

3.2. Lithium-ion battery performance

The test results are analyzed in Fig. 8 and Fig. 9.

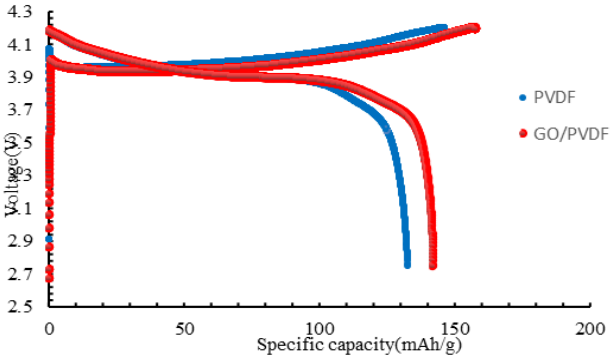

Fig. 8. Lithium-ion battery first charge and discharge curve (color online)

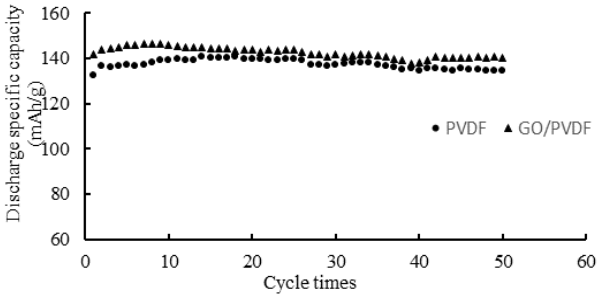

Fig. 9. Cyclic performance of lithium-ion batteries

Fig. 8 shows the first charge discharge curve of the battery assembled with PVDF fiber membrane and GO/PVDF(GO:0.5%) fiber membrane. High discharge platform means that more energy can be released and more work can be done under the same current. Larger discharge capacity means longer discharge duration. It can be seen from the Fig. 8 that both batteries have a stable charging and discharging platform. The first discharge specific capacity of the battery with GO/PVDF fiber membrane as the membrane is up to 141.9mAh/g, while the first discharge specific capacity of the battery assembled with PVDF fiber membrane is 132.6mAh/g. No matter the discharge platform or specific capacity, GO/PVDF fiber membrane is superior to PVDF fiber membrane assembled battery.

Fig. 9 shows the cycle stability of the battery assembled with the two membranes. It can be seen that the specific capacity of the assembled battery with GO/PVDF fiber membrane is always higher than that with PVDF fiber membrane throughout the cycle, which shows that the addition of GO significantly improves the cycle performance of the cell. After 50 cycles, the specific discharge capacity of the battery assembled with PVDF fiber membrane is 134.7mAh/g, while the specific

discharge capacity of the battery assembled with GO/PVDF fiber membrane is still 140.3mAh/g, and the attenuation rate is only 1.1%, showing good battery cycle performance.

In summary, it is known that GO/PVDF fiber membranes are more suitable for lithium ion batteries than PVDF fiber membranes.

4. Conclusions

In this paper, GO/PVDF composite nanofiber membranes were prepared by electrospinning. It was found that the amount of GO should be appropriate, too large may affect the normal filament formation of electrospun fiber. After adding GO, the surface roughness of the fiber increased obviously, and the fiber was no longer smooth and straight. With the increase of the mass of GO, the average diameter of the fiber increases, the uniformity of the diameter becomes worse and the diameter distribution becomes wider. The addition of GO reduces the crystallinity of the GO/PVDF membrane, which is conducive to improve its ionic conductivity, but the strength of the fiber membrane will decrease.

The button type lithium-ion batteries were assembled with GO/PVDF fiber membrane as separator, and the performance of the battery was measured. The results show that the GO/PVDF fiber membrane is superior to the PVDF fiber membrane assembled battery in terms of discharge platform or discharge specific capacity. And the addition of GO significantly improves the cycle performance of the battery. In conclusion, the GO/PVDF fiber membrane is more suitable for lithium-ion battery than the PVDF fiber membrane.

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