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Short communication

Polyvinylidene fluoride membrane by novel electrospinning system for separator of Li-ion batteries

Cuiru Yang [a,*], Zhidong Jia [a,b], Zhicheng Guan [a,b], Liming Wang [a,b]

[a] Department of Electrical Engineering, Tsinghua University, Beijing 100084, China
[b] Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China

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ABSTRACT

The remarkable characteristics of nanofibers mats electrospun are large surface area to volume ratio and high porosity, which are crucial to increase the ionic conductivity of membrane full of liquid electrolyte, in this aspect, electrospinning is prior to the other methods, such as dry method, wet method, etc. Therefore, fabricating the separator of Li-ion batteries by electrospinning is potential and promising. The PVDF membranes were fabricated by electrospinning. The experiment demonstrated that the main deficiency in the fabricating separators process by electrospinning was low mechanical property, which induced partial short circuits inside the cells. Several methods were presented to enhance the mechanical strength. The experiments demonstrated that the higher the solution concentration was, the stronger the mechanical strength was, and the higher the voltage was, the stronger the mechanical strength was. Additionally, the spherical hat collection target instead of conditional plane target was applied in the electrospinning system, as a result, the thickness of the membrane was more uniform and the fiber diameter was also more uniform. Therefore, the charge and discharge capacity of the coin type cell composed of the separator collected by spherical hat target exceeded the plane target, and the electrospinning separators exceeded the commercial polypropylene separator.

1. Introduction

Polyolefin microporous membranes have been used as major commercial separators for the lithium-ion battery. Obviously, the conventional separators have quite suitable properties, i.e., Chemical stability, suitable thickness, and mechanical strength [1]. However, low porosity of about 40% resulted from the semi-crystalline structure and melt blowing technics, and the large difference of the polarity between the nonpolar polyolefin separator and the highly polar liquid electrolyte, which result in low wettability, lead to an increase in cell resistance. This nature of polyolefin separators would restrict the performance of the lithium-ion batteries [2,3].

Therefore, many researchers developed novel methods and applied different materials to fabricate the membranes for the separators of Li-ion batteries. The fibrous webs can be formed by a wet process such as a paper-making process [4,5], a solution extrusion method using a spinning jet [6] and wet-laid method [5,7,8] or by a dry process such as a melt blowing method [9,10]. In order to reduce thickness while still remaining good mechanical strength, an electrospinning method had been adopted to prepare the highly porous non-woven separators by applying a high voltage between the solution capillary jet and the membrane-collecting substrate, and the PVDF membrane were electrospun in the experiments [11,12]. Choaz [2] fabricated Polyacrylonitrile nanofiber-based nonwoven separator for Lithium-ion battery by electrospinning. However, the conventional electrospinning system [13], which used the plane target as the collector, gained the uneven electrospun membrane. The deposition of the fiber can be controlled by change electric field distribution [14–17].

In this paper, the spherical hat collector applied in the electrospinning can collect the uniform fiber mats, which were used to fabricate the separator of Li-ion batteries after secondary treatments. The secondary treatments technics were improved by soaking the membrane by ethanol, making it flat and pressing while heating. Then, the separators were used to assemble the coin type cell which was composed of $LiFePO_4$ as the anode, lithium foil as the cathode. The experiments demonstrated that the charge and discharge properties of initial ten times cycles of the cells assembled by electrospun separators were prior to the commercial polyolefin separators.

* Corresponding author at: Nanshan District Xili University Town Tsinghua University L110, Shenzhen 518055, China. Tel.: +86 755 26036693; fax: +86 755 26036080.
E-mail address: yangcr06@mails.tsinghua.edu.cn (C. Yang).

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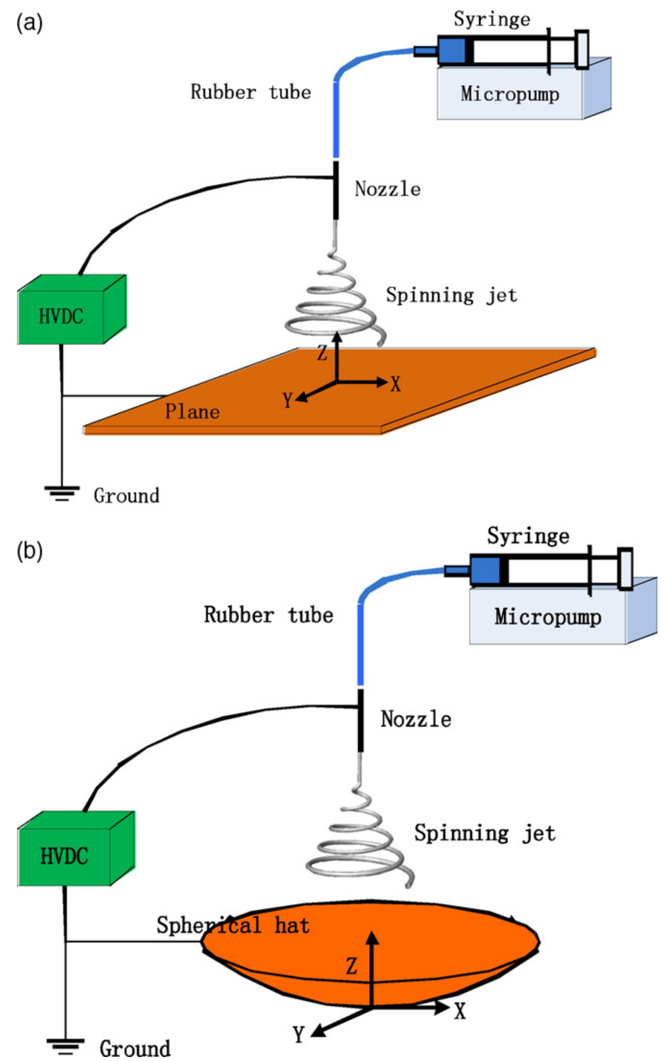

Fig. 1. (a) Conventional electrospinning system with plane collection target, (b) novel electrospinning system with spherical hat collection target.

2. Experimental

Poly(vinylidene fluoride) (PVDF) is a favorable dielectric and easy to be electrospun, and it has strong mechanical strength and high thermal stability, so it was chosen for the electrospinning material. The polymer solution was prepared by dissolving 30 g of PVDF (Solubility exponent of 24, Kureha Chemical Industry Co., Ltd) in 200 ml of *N*,*N*-dimethylformamide (DMF, Tianjin Hongyan Chemical Industry Co.), and the PVDF/DMF solution was heated to 75 °C for 96 h by electric-heated thermostatic water bath.

The electrospinning experimental systems were illustrated in Fig. 1. Fig. 1a is the sketch-map of conventional electrospinning system with plane collection target (40 cm × 40 cm, labeled as P). Fig. 1b is the novel electrospinning system with spherical hat collection target (the target heights are 4.5 cm, the spherical radius is 25 cm, labeled as S). The parameters of spherical hat target were designed in Reference [18]. The coordinates were drawn in the figure to facilitate to explain the latter results, and the point of intersection of the needle prolonged line and the target is selected as the origin. The electrospinning parameters and conditions were listed in Table 1.

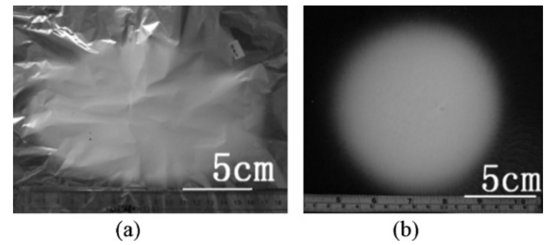

Fig. 2. Deposition patterns with plane collection target and spherical hat collection target after 70 min. (a) 3#. (b) 7#.

The electrospun fiber mats cannot directly used for the separators of Li-ion batteries. They must be secondary treated. All secondary treatments were processed according to following method: first, put the electrospun membrane on the plane glass sheet, then soak the membrane by ethanol and make it flat, third, the membrane was pressed by another plane glass sheet, forth, the second plane glass sheet was pressed by a stainless steel cylinder to provide some pressure for the membrane to make it flatter, thinner and more close-grained. Only after secondary treatments, can the membranes be used as the separator of Li-ion batteries. The 3#a and 7#a corresponding to the 3# and 7# after secondary treatment respectively, were used to assemble the coin type cell. The celgard 2500 separator was used to compare with the electrospun separators. The coin type cell was composed of $LiFePO_4$ as the anode, lithium foil as the cathode.

3. Results and discussion

Fig. 2 shows the deposition patterns of the membranes electrospun with plane collection target and spherical hat collection target after 70 min. In Fig. 2, 3# and 7# were taken for example and Fig. 2a and b were corresponding with 3# and 7#. It indicated the plane target would collect elliptical fiber mat (R_x = 11 cm, R_y = 17 cm, wherein, R_x and R_y were the sizes of the *X* and *Y* axis respectively according to the coordinates of Fig. 1a), and the spherical hat targets could collect circular fiber mats (the diameter was 13 cm).

The morphology of electrospun separators was obtained by SEM observation. As shown in Fig. 3a, the red circles showed the generated silica, and the porosity (as black circles in Fig. 3a) increases because the two phases of PVDF and SiO_2 cannot dissolve each other. Fig. 3b and c were the SEM images after secondary treatments for 3# and 7#, which indicated that some fibers adhered to

Table 1
Several electrospinning conditions

Number	Target	Concentration (%)	Distance (cm)	Rate (ml h^{-1})	Voltage (kV)
1#	P	12.5	15	1	19
2#	P	10% PVDF + 2.5% SiO_2	15	1	19
3#	P	15	15	1	19
4#	P	15	15	1	17.5
5#	P	15	15	1	16
6#	P	15	15	1	13.2
7#	S	15	15	1	19

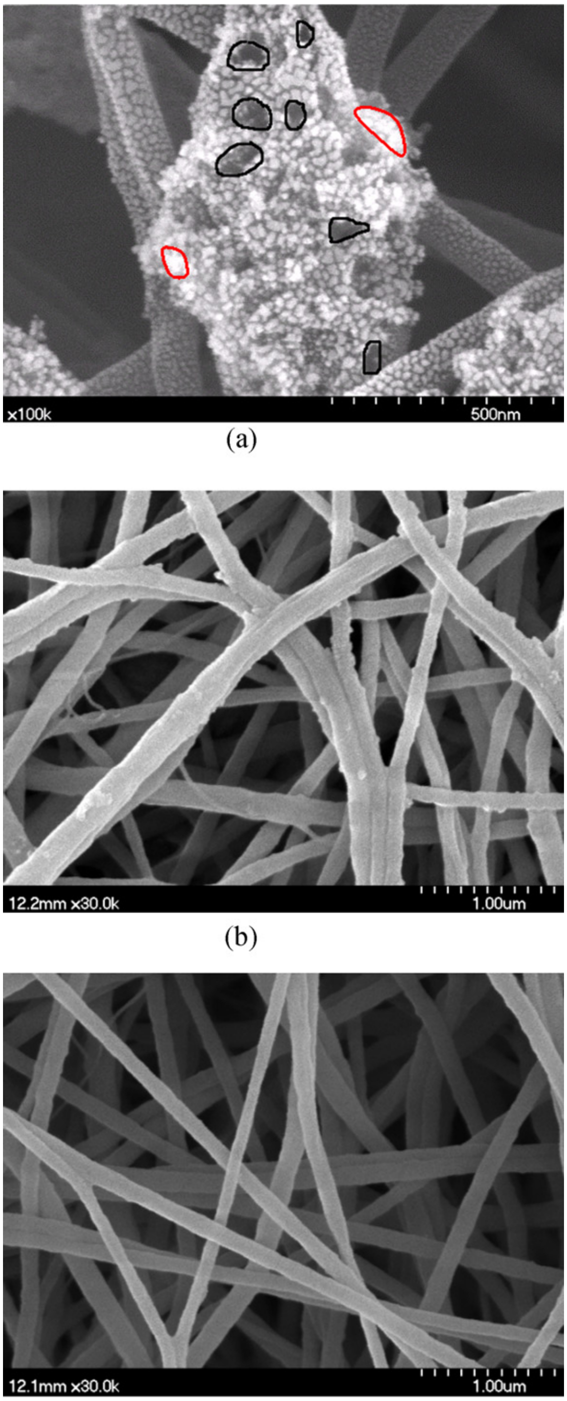

Fig. 3. SEM images of electrospinning membranes. (a) 2#. (b) 3#a. (c) 7#a.

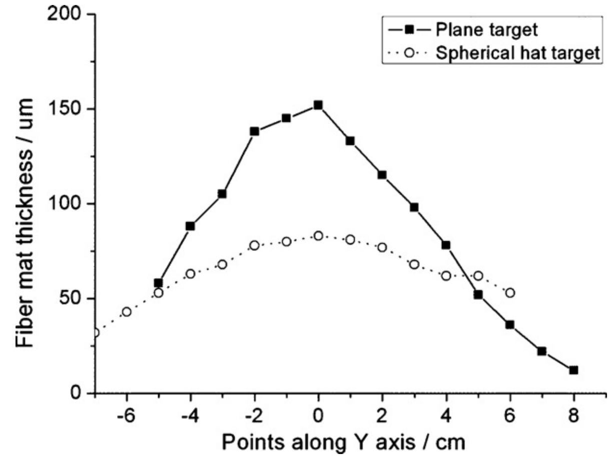

Fig. 4. Thickness of fiber mats with various collection targets after 70 min.

each other due to thermal effect and the fiber diameter of 7#a was more uniform than 3#a.

The distribution of the electrospun fibers was not uniform in the collection region with different collectors. It behaved with the uneven thickness of the collecting fiber mats. Fig. 4 shows the differences of fiber mats collected for 70 min with different collection targets. The thickness values were gained by measuring the points every 1 cm along a coordinate *Y* axis with a micrometer. Obviously, the thickness of fiber mat collected with plane target was greatly uneven in wide area. The spherical hat target can collect uniform fiber mats in large area.

The range of fiber diameters altered when the collection target was changed. The electrospun fibers were observed with a scanning electron microscope, and from the resulting SEM images the diameters were measured with IMAGEJ software [19] to form a statistical plot such as Fig. 5. It shows that the diameters of fibers collected with plane target were increasing with the collecting time, and the diameters of fibers collected with spherical hat target kept stable. Additionally, it is found that the diameters of fibers collected with spherical hat target were thinner than the plane target at any time. The continuous fibers fell onto the target surface and stack layer upon layer to form fiber mats, so the fiber characteristics of mats collected at different electrospinning times can reflect the fiber characteristics of inner different layer of mats collected for long time. Therefore, the inner fiber diameters are uneven for the mats gained from the plane target, such as Fig. 5a, and the diameter was increasing from bottom to the surface with the collecting time. The inner fiber diameters were uniform for the mats gained with spherical hat target, such as Fig. 5b.

From Table 2, we can find the fiber mats electrospun with different parameters had varied mechanical properties. Comparing 1# and 3#a, it was found the higher the polymer solution concentration was, the stronger the tensile strength was. As for 2#, the mechanical strength was the most weakest in all samples. It shows the silica does not play the natural enhancing the mechanical strength role, one of possible reason was the silica contents was low, another was that the silica generated, such as red circles in Fig. 2, at the same time, the porosity (as black circles in Fig. 2)

Table 2
Mechanical properties of varied samples

	Sample						
	1#	2#	3#a	4#	5#	6#	7#a
Tensile strength (MPa)	1.783	0.389	6.265	5.36	2.922	1.78	6.895
Elongation at break (MPa)	35.225	15.21	34.603	47.3	73.732	36.01	48.756

Table 3
Porosities of varied sample

	Sample									
	Celgard 2500	1#	2#	3#	3#a	4#	5#	6#	7#	7#a
Porosity (%)	55	127	136	125	69	120	116	108	130	76

increases because the two phases of PVDF and SiO_2 cannot dissolve each other. If the problem of generating can be solved, the silica filler should improve the mechanical strength of the mats, which will be one of promising methods in next work. Comparing 3#a, 4#, 5# and 6#, it was found that the lower the electrospinning voltage was, the weaker the tensile strength was. The primary reason was in the case of same solution concentration, the lower electrospinning voltage would lead to thick fiber diameter [20–24]. The thicker the fiber diameter was, the weaker the tensile strength was. Comparing 3#a and 7#a, it was found the more uniform the fiber diameter was, the stronger the tensile strength was.

Table 3 shows the porosity of varied samples, Generally speaking, the thinner the fiber diameter was, the higher the porosity was.

The rate capabilities of the separators were investigate by applying constant current charge and discharge. The cells were charged up to 4.2 V, then discharged to 2.5 V at a 0.1 C rate (1 C = 170 mA g^{-1}). Only the initial ten times the charge and discharge properties were observed. The results of rate capability tests are presented in Fig. 6. The electrospun separators show excellent rate capabilities. The

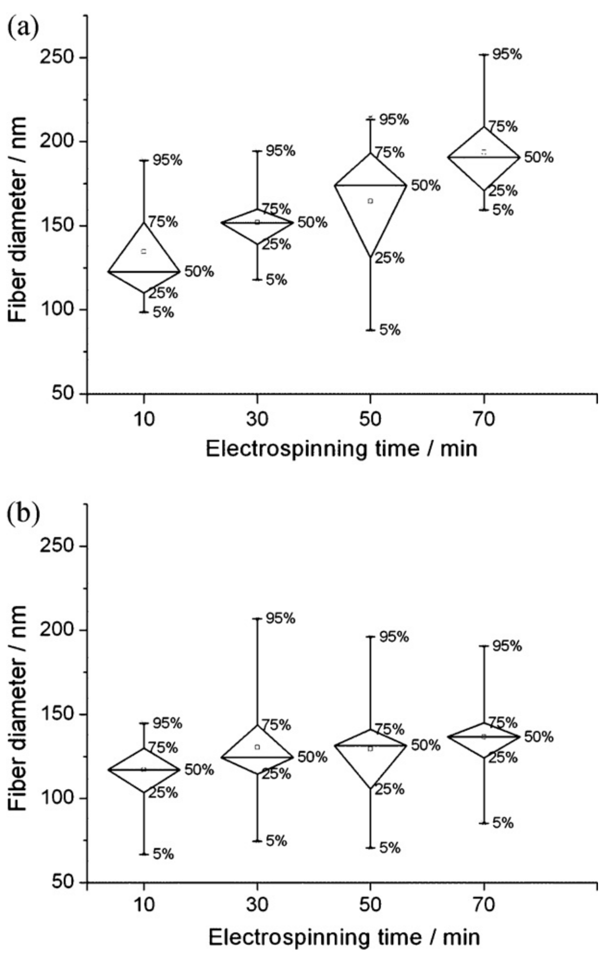

Fig. 5. Fiber diameters of various electrospinning time with (a) plane target and (b) spherical hat target.

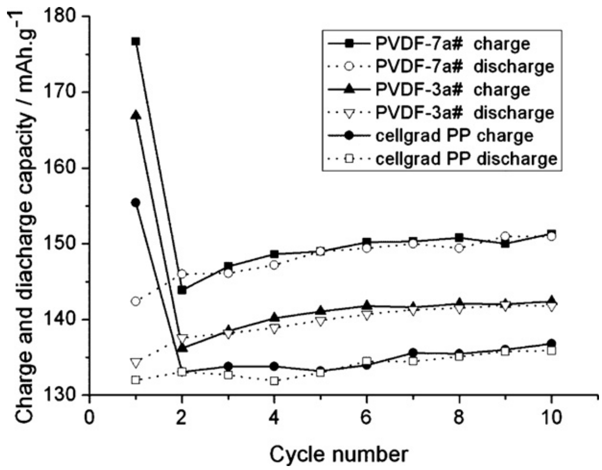

Fig. 6. Charge and discharge properties of initial ten times cycles.

capacities of PVDF-7#a and PVDF-3#a were both higher than the celgard 2500, and the PVDF-7#a had the highest capacity. One of the reasons should be that the higher the porosity was, the higher the capability was. Another probable reason was the stress in secondary treatments to make the separators flatter to decrease the inner resistance.

4. Conclusion

Due to the intrinsic disadvantages of conventional electrospinning system with plane target, we develop a novel electrospinning system with spherical hat target. Therefore, the membranes with uniform thickness and fiber diameter were collected to fabricate the flatter and high porosity separators. The experiments demonstrated that the higher the solution concentration was, the stronger the mechanical strength was; the thinner the fiber diameter was, the stronger the mechanical strength was; and the more uniform the thickness and the fiber diameter were, the stronger the mechanical strength was. The separator was confirmed to have high capacity by the rate capabilities study at a 0.1 C rate. Therefore, the novel developed electrospinning separators can be potential and promising candidate for separators of Li-ion batteries.

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