Preparation of a Novel UHMWPE Lithium Battery Separator by Electrospraying Method

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Abstract: In this paper, an ultra high molecular weight polyethylene (UHMWPE) lithium ion battery composite separator was successfully prepared via the electrospraying technique. First, the optimal electrospraying parameters of Polyvinylidene fluoride (PVDF), mass fraction of PVDF 3wt% and electrospraying voltage 21kV, were successfully determined by adjusting the effect of voltage and concentration of PVDF solution. Then the composite separator was prepared by electrospraying PVDF particles on the UHMWPE film. Finally the porosity rate, thermal stability and charge and discharge properties of the separator were analyzed. The analytical results show that the porosity rate of the composite separator is increased from 46.5% to 73.1%, and the heat shrinkage of the separator in the longitudinal is reduced from 2.6% to 1.3%. The first specific discharge capacity of the composite separator increases by 5.8%, and the separator has a good cycle stability after 50 cycles.

1. Introduction
Because the lithium battery has excellent performance, such as high energy density, high operating voltage, long cycle life, low self-discharge rate [1], the battery is widely used in electronic products including phone, laptop and so on.

As an important component of the lithium battery, the separator which is between the positive and the negative has the effect to provide a microporous channels for the ion mobility [2]. The capacity, cycle stability and safety of the battery are directly affected by the quality of the separator, that is to say, if there is no high-quality separator, the excellent battery will not exist [3]. Electrospraying is a kind of processing method to prepare polymeric particle via a high-voltage electrostatic field. During the electrospraying process, polymeric parameter, solution parameter, voltage and receiving distance have influence on the size of the particle and morphology [4-6]. Hu prepared the biodegradable polymeric microspheres by the electrospraying which was used as the drug carrier [7]. Cao deposited the nano titanium dioxide on the surface of the purification materials to prepare the sandwich materials which possess a good antibacterial properties [8]. Yin et al applied the electrospraying technique to prepare the Si/C nanomicrospheres which can be used as the positive material of the lithium battery, his research results show that the nanomicrospheres have the high reversible specific capacity and excellent cycle property [9]. Volvo prepared a metal oxide/PVDF nanocomposition to modify the negative material of the lithium battery [10]. Nanoparticle-on-nanofiber hybrid membranes were prepared by electrospraying of SiO2 dispersions and electrospinning of polyvinylidene fluoride (PVDF) on PP separator.
simultaneously, as the separator of the lithium battery, the pore rate and thermal stability of this separator has got significant improvement [11].

The research by electrospaying of organics to modify the UHMWPE separator has not been reported. In this article, PVDF particles was electrospayed on the surface of the commercial UHMWPE separator to prepare a novel PVDF/UHMWPE composite separator. The analytical results show that the porosity rate of the composite separator is increased from 46.5% to 73.1%, the heat shrinkage of the separator in the longitudinal is reduced from 2.6% to 1.3%, the first specific discharge capacity of the composite separator increases by 5.8%, and the separator has a good cycle stability after 50 cycles.

2. Experimental Section

2.1 Chemical
Polyvinylidene fluoride: product 44080, molecular 534000, Alfa Aesar; Acetone: AR, from Beijing Chemical Works, China; N, N- dimethylformamide: AR, from Beijing Chemical Works, China; UHMWPE separator: SG208, molecular weight 1800000, from HeBei Gellec New Energy Material Science&Technolooy Co., Ltd., China

2.2 Preparation of PVDF particles
The PVDF solution was prepared by dissolving 3wt% PVDF in DMF/acetone (2:3 by weight), which was stirred at 60℃ for 8h. The PVDF mass fraction of the solution were 1 wt%, 3 wt%, 5 wt%, 7 wt%, 9 wt%, respectively. After ultrasound (power 150W) treatment for 30 min, PVDF particle was electrospayed on the surface of UHMWPE film. The average diameter of particle was analyzed by the RISE-2008 laser particle size analyzer [12].

2.3 Preparation of composite separator
The UHMWPE composite separator was prepared via electrospaying the different contents of PVDF particle on commercial UHMWPE separator under the optimum condition.

2.4 Characterization and performance test of UHMWPE composite separator
The morphology of UHMWPE composite separator was determined by a S-4800 field emission scanning electron microscope (SEM, S-4800, Hitachi). The porosities of the separators were analyzed by using n-butanol uptake tests. The porosity was calculated using the following equation:

\[
\text{Porosity} \% = \frac{w_2 - w_1}{\rho V} \times 100
\]

Where \(w_2\) and \(w_1\) are the weights of wet and dry separators, respectively, \(\rho\) is the density of n-butanol, and \(V\) is the geometric volume of the separator.

The dimensional stability of the separators were determined by thermal shrinkage test at 120 ℃ for 1h. The shrinkage of separators was calculated according to the following equation:

\[
\text{Shrinkage} \% = \frac{D_0 - D}{D_0} \times 100
\]

Where \(D_0\) and \(D\) are the diameters of separators before and after heat treatment, respectively.

The coin-type cells were assembled by sandwiching the composite separators between LiFePO4 and Li metal electrodes in a glove box filled with dry argon. The cycle performance of cells fabricated with different separators were examined under the constant current mode at 0.2C with the operating voltage ranging from 2.5V to 4.2V using a cycle test instrument (CT2001A, Wuhan Jinnuo Electronics, China).

3. Results and discussion

3.1 Effect of concentration on the PVDF solution electrospraying
Concentration of a solution is an important parameter of electrospraying. The surface tension and viscosity can be adjusted by changing the concentration of PVDF, which will affect the size of the particles [17]. Due to the low entanglement of molecular chains in the 1 wt% PVDF solution, the jet was
unstable under electrostatic force and surface tension, and the droplets occurred more frequently\[^8\]. From the Figure.1, we can see that there were smaller and uniform particles in the concentration of 3 wt% PVDF, the particle size became larger in the concentration of 5 wt% PVDF, however, the concentration increased to 7-9 wt%, the electrostatic spraying process was difficult due to a high viscosity of the solution.

3.2 The influence of voltage on the electrospraying

According to the Scaling law of Hartman\[^{13}\], the diameter of electrospraying particles is inversely proportional to the current, the greater the current, the smaller the particle. And current is directly proportional to the voltage between the syringe and receiving device, the greater the voltage, the smaller the spray particle diameter. Table. 1 shows that when voltage increases from 13 kV to 21 kV, its average particle diameter reduce from 3.83μm to 1.70μm. We conclude from Figure.2 that there is reunion content at 13kV, and no reunion at 21kV. So we choose 21 kV as spraying voltage.

![Figure 1: SEM images of PVDF particles with different solution concentration](image1)

![Figure 2: SEM images of PVDF particles with different electric voltage](image2)

| Voltage (kV) | Concentration (wt%) | Spraying distance (cm) | Average particle diameter (μm) |
|-------------|---------------------|------------------------|-------------------------------|
| 13          | 3                   | 15                     | 3.83                          |
| 15          | 3                   | 15                     | 3.56                          |
| 17          | 3                   | 15                     | 2.94                          |
| 19          | 3                   | 15                     | 2.12                          |
| 21          | 3                   | 15                     | 1.70                          |
3.3 Porosity of composite separator
The test of composite separator porosity results with different quantities of PVDF particles spraying on UHMWPE separator surface are shown in Table 2. From Table 2, we can conclude that the porosity of composite separator is between 46% ~ 74%. When spraying time is 2 min, the maximum porosity is 73.1%, increased by 57.2% compared with the UHMWPE separator, there is a maximum porosity because of pore jams formed with the increase of particles.[11]

Table 2 The porosity of Composite Separator

| Spraying time /min | The mass of dry separator M1/g | The mass of wet separator M2/g | The volume of dry separator V/cm³ | Porosity % |
|-------------------|-------------------------------|-----------------------------|-------------------------------|------------|
| PVDF 0min         | 0.0022                        | 0.0036                      | 0.0036                        | 46.5       |
| PVDF 2min         | 0.0023                        | 0.0045                      | 0.0036                        | 73.1       |
| PVDF 4min         | 0.0025                        | 0.0043                      | 0.0036                        | 59.8       |
| PVDF 6min         | 0.0028                        | 0.0042                      | 0.0036                        | 46.5       |

3.4 Dimensional stability
We also studied the thermal stability of the PVDF/UHMWPE composite separator compared with commercial UHMWPE separator by calculating the dimensional change after heat treatment. Figure 3 shows that the UHMWPE separator exhibits relatively poor thermal stability and the longitudinally thermal shrinkage is about 2.6% at 120°C after 1h treatment. In contrast, the composite separator after spraying 6 min shows improved thermal stability and displays only 1.3% shrinkage at the same condition. The transverse thermal shrinkage of the commercial UHMWPE separator and the composite separator have no significant change.

Figure 3 the Dimensional Stability of Composite Separator
Table 3: The Heat Shrinkage of Composite Separator

| Spraying time /min | Transverse shrinkage /% | Longitudinally shrinkage /% |
|--------------------|-------------------------|-----------------------------|
| PVDF 0min          | 0.6                     | 2.6                         |
| PVDF 2min          | 0.6                     | 1.9                         |
| PVDF 4min          | 0.6                     | 1.6                         |
| PVDF 6min          | 0.6                     | 1.3                         |

3.5 Charge and discharge performance of composite separator

The first discharge capacity curve of composite separator was shown in Figure 4. It shows that the first discharge capacity of UHMWPE separator is 116.67 mAh.g⁻¹. When the spray time of PVDF particles is for 2 min, 4 min, 6 min, respectively, the first discharge capacity is 122.47 mAh.g⁻¹, 120.26 mAh.g⁻¹, 116.68 mAh.g⁻¹, respectively, we can see that the largest first discharge capacity appears in the spray time for 2 min, which increase by 5.8% than that of common UHMWPE separator. However, the first discharge capacity decreases with the increasing of spraying time. This is plausibly because that small amount of PVDF particles on the surface of UHMWPE can improve the porosity of the separator and let more lithium ions go across, more quantity of PVDF particles on UHMWPE surface not only will decrease the porosity of the separator and may clog pores on the surface of the separator, which results in the decrease of porosity and a reduction of discharge capacity, therefore, the best spray time is for 2 min [11].

Figure 5 is the cyclic stability of composite separator by electrostatic spraying PVDF particles on UHMWPE separator in different time. From which we see a good cyclic stability exists after 50 times charging and discharging test.

4. Conclusion

Ultra-high molecular weight polyethylene composite separator was made through electrospraying
technology by loading PVDF particles on the surface of ultra-high molecular weight polyethylene separator. The separator has higher porosity and better dimensional stability than that of a commercial UHMWPE separator. The best parameters of spraying conditions are, a solution concentration of 3 wt %, a spraying voltage of 21 kV, a receiving distance of 15 cm. Tests of lithium ion battery bearing the composite separator show that various properties of composite separator is excellent, and the battery discharge capacity increased by 4.2% for the first time. After 50 times charging and discharging test, the battery exists a good cycle stability.

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