



# Polyphenylene sulfide nonwoven-based composite separator with superior heat-resistance and flame retardancy for high power lithium ion battery

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## ABSTRACT

In this study, a new alternative nonwoven based on engineering plastic polyphenylene sulfide (PPS) was explored as the support to construct high performance and safety separator for the first time. By the method of physical coating polymer poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and inorganic nanoparticle SiO<sub>2</sub> on the support, the designed composite separator was successfully obtained for lithium ion battery. Systematic investigations ranging from physical properties, thermal properties to electrochemical performances were carried out. It was found that compared with commercialized polyolefin separator, PPS nonwoven-based composite separator possessed higher porosity, air permeability, improved electrolyte wettability and electrolyte uptake, thus being helpful for lithium ion transfer between electrodes and increasing the ionic conductivity. These behaviors accordingly endowed battery with superior discharge capacity at various discharge current rates from 0.2 C to 2 C. Moreover, the composite separator was observed to exhibit excellent dimensional stability even after thermal treatment at 250 °C and present good flame retardant ability. The afore-mentioned outstanding performances of PPS nonwoven-based composite separator would shed light on the development of high power lithium ion battery.

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## 1. Introduction

In the last decades, lithium ion battery (LIB) has been vigorously developed, with applications expanding from portable electronic devices to electric vehicles and energy storage systems, which brings forward higher request for the power density of LIB [1–3]. However, two challenges namely safety issue and the limitation of cell performance must be considered when exploiting high power battery [4,5]. Separator, as an indispensable component in LIB, is physically placed between cathode and anode with an important role in blocking electron transfer and preventing short-circuit. Surely, separator should be deemed as the key to solve safety problem [1]. Besides, separator must allow Li<sup>+</sup> to pass through fluently during battery work [6]. This behavior determines the

degree of ohmic polarization in LIB, thus having a significant effect on the improvement of cell performance [7,8].

Polyolefin separator has occupied a leading position in commercialized LIB. However, some drawbacks cannot be ignored such as poorer heat-resistance, lower porosity, and inferior electrolyte wettability. These make polyolefin separator fail to meet the demands of high power battery [7]. Recently, nonwoven-based separator has raised considerable attention owing to its low cost and high porosity. In contrast to the rather limited options of polymers to fabricate polyolefin separators, nonwoven enjoys the unique merit of diverse starting materials [7]. Therefore, it is a preferential option to employ high temperature resistant polymer-based nonwoven to construct separator for maintaining superior dimensional stability and achieving high power LIB [9]. However, the reported nonwovens are mainly based on some limited polymeric materials such as poly(ethylene terephthalate) (PET) [1], polyimide (PI) [10] and cellulose [4,11]. Meanwhile, their flame retardant abilities are relatively insufficient [9]. Hence, it is

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imperative to explore novel nonwoven based on other high performance engineering plastic to build separator for further improving comprehensive performance.

Engineering plastic polyphenylene sulfide (PPS) has been extensively explored owing to the unique advantages including thermal stability, chemical resistance, flame retardancy as well as insulation property [12]. These lead us to envision the potential of separator constructed by PPS nonwoven to guarantee battery safety. To the best of our knowledge, related studies have not been reported. However, PPS nonwoven cannot be directly applied as separator due to large pore size together with uneven pore size distribution, or else leading to the occurrence of self-discharge or unstable current distribution in LIB [8]. Therefore, in this contribution, we developed PPS nonwoven-based composite separator by modifying PPS nonwoven through physical coating polymer poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and inorganic nanoparticle SiO<sub>2</sub>, where the coating materials were helpful for the improvement of electrolyte wettability [13] when optimizing pore size and distribution. Subsequently, systematic investigations for separator ranging from morphology and structure, wettability and electrolyte uptake, thermal stability and flame retardancy to electrochemical property and cell performance were carried out. To evaluate the performance of composite separator, commercialized polyolefin separator PP/PE/PP was utilized as the control group. In addition, detailed analysis and explanations were given to all the results, and the relationships between structures and properties were built accordingly.

## 2. Experiment

### 2.1. Materials

Polyolefin multilayer separator (PP/PE/PP, Celgard 2340) was received from Celgard Company. Polyphenylene sulfide (PPS) nonwoven (~80 μm) was produced by melt-blown method in our lab. Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP, M<sub>w</sub> = 455000) and inorganic nanoparticle SiO<sub>2</sub> (15 nm) were respectively purchased from Sigma-Aldrich and Aladdin. Acetone and *N,N*-dimethylformamide (DMF) were obtained from Sino-pharm Chemical Reagent Co., Ltd and used without further purification. LiFePO<sub>4</sub> cathodes were acquired from Shenzhen Kejing Star Technology Co., Ltd. Lithium metal anodes and liquid electrolyte 1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1) (v/v) were obtained from Shenzhen Biyuan Electronics Co., Ltd.

### 2.2. Preparation of composite separator

PPS nonwoven-based composite separator was prepared by a dip-coating method according to the previous literature [14]. Firstly, PVDF-HFP and SiO<sub>2</sub> were added into acetone and DMF mixed solvent at a constant ratio (SiO<sub>2</sub>: PVDF-HFP: acetone: DMF = 3: 5: 45: 5 by weight). The mixture was stirred with mechanical agitation for 2 h at 60 °C. Subsequently, PPS nonwoven was dipped into the dispersed solution for a certain time and then taken out. The coated separator was sequentially dried in fume hood at room temperature and in vacuum at 50 °C for 24 h to completely remove residual solvent. The obtained PPS nonwoven-based composite separator was hot-pressed prior to use to keep flat.

### 2.3. Physical characterization of separators

The surface morphology of composite separator was examined employing a scanning electron microscopy (SEM) (JEOL JSM-6510LV). Before examination, a thin Au film was vacuum-deposited on the surface of sample. The porosity of separator

could be estimated by *n*-butanol absorption method [14]. To evaluate the permeability of separator, Gurley densimeter (America, Gurley 4110N) was utilized to measure Gurley value (s/100 cc) which was the time for a determined volume air to pass through membrane with a fixed area under a given pressure.

To determine the electrolyte wettability of membrane, the immersion-height was recorded every 20 min after immersing one end of separator in liquid electrolyte. The electrolyte uptake of separator was determined using the following equation (1):

$$\text{Electrolyte uptake (\%)} = \frac{W - W_0}{W_0} \times 100\% \quad (1)$$

where  $W_0$  and  $W$  are the weights of separator before and after soaking in the liquid electrolyte for 30 min, respectively.

The thermal property of separator was carried out by differential scanning calorimetry (DSC) in the temperature range of 50 °C–300 °C at a heating rate of 10 °C/min using a DSC 204 F1 (NETZSCH). The thermal shrinkage of separators (original size: 2.5 cm × 2.5 cm) was evaluated by measuring their (area-based) dimensional change after treatment for 0.5 h at different temperatures changed from 120 °C to 250 °C. The flame retardant ability was investigated by combustion test of separator. The stress-strain curves of membranes were conducted on an Instron universal tester with a strain rate of 30 mm/min. The samples were cut into 3 cm width × 10 cm length for testing.

### 2.4. Electrochemical analysis

The ionic conductivity of separator was gained by measuring electrochemical impedance spectroscopy (EIS) on Autolab (PGSTAT302N) within the frequency range from 0.1 Hz to 100 kHz under a voltage amplitude of 10 mV. For test, SS/separator/SS cells (SS = stainless steel) were assembled and activated by filling liquid electrolyte. The ionic conductivity ( $\delta$ ) was calculated based on equation (2):

$$\delta = \frac{d}{RA} \quad (2)$$

where  $R$  is the bulk resistance of separator determined from the Nyquist plot,  $d$  and  $A$  are the thickness and area of separator, respectively. To analyze the interfacial resistance between separator and electrode, Li/separator/Li cells were assembled and activated by liquid electrolyte. Then impedance data were recorded on Autolab in the frequency range from 0.1 Hz to 100 kHz under a voltage amplitude of 10 mV. To obtain the electrochemical window of separators, linear sweep voltammograms (LSV) curves of SS/separator/Li cells (SS = stainless steel) were conducted from 2.0 V to 6.0 V under the scan rate of 1 mV/s.

### 2.5. Cell assembly and performance characterization

Lithium ion half cell (2016-type coin) was fabricated in an argon filled glove box by placing liquid electrolyte soaked separator between LiFePO<sub>4</sub> cathode and lithium metal anode. Cell performances were conducted on a LAND battery testing system (Wuhan LAND Electronics Co., Ltd, China) with cut-off voltages of 4.3 V for the upper limit and 2.5 V for the lower limit. The charge/discharge curves were carried out by varying the charge/discharge current density from 0.2 C/0.2 C to 2 C/2 C. To examine cycling performance, cells were cycled 100 times at a fixed charge/discharge current density 0.5 C/0.5 C.

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