



# A sandwich-like composite nonwoven separator for Li-ion batteries



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## ABSTRACT

In this paper, the background, current research status and problems of separators for Li-ion batteries were reviewed first. Then a novel sandwich-like type of composite nonwoven separators was prepared to improve the performance of composite nonwoven Li-ion battery separators by combining SiO<sub>2</sub>/PVDF-HFP membranes with PVDF-HFP dipped PP nonwoven fabric. The physical and electrochemical properties of the composite separators were measured and analyzed. It is found that the mean pore size of the composite separators was in the range of 100 to 300 nm with maximum pore size less than 2 μm. The composite nonwoven-based separators possessed higher electrolyte uptake, stronger thermal stability, better wettability and lower interfacial resistance than the commercial PE separator. The batteries assembled with composite nonwoven separators showed stable cycling performance and improved rate performance. The composite nonwoven separators are expected to be a promising alternative to commercial PE separator.

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## 1. Introduction

The Li-ion battery has been the major power source for various electronic devices like laptops, digital cameras, and mobile phones because of its higher energy density, longer service life, lower self-discharge rate and higher operational voltage than conventional batteries[1–3]. However, safety concerns, unsatisfactory rate performance and high cost still limit its application in hybrid electric vehicles (HEV) and electric vehicles (EV)[4–6].

A separator is a kind of porous membrane placed between an anode and a cathode to keep them apart to prevent internal short circuits and at the same time allow rapid transport of ions[7]. An ideal separator should have a zero ionic resistance, however in practice a low ionic resistance can be achieved by a high porosity. Nowadays, microporous polyolefin separators such as polypropylene (PP) and polyethylene (PE) separators are commercially used as Li-ion battery separators due to their superior chemical stability, significant mechanical property and thermal shut-down performance[8,9]. The average pore size of traditional polyolefin-based separators is normally in the range of 0.03 μm to 0.1 μm with the porosity falling between 30% and 55%[7]. The small pore size, relatively low porosity and poor wettability with polar liquid electrolyte restrict its cell performance[1]. In addition, the processes used to create pores in commercial polyolefin separators

require precise stretching of an extruded thin film. Heat exposure to these stretched separators initiates re-coiling of the elongated polymer chains, observed as shrinkage or the shape memory effect, causing stress to build at the fixed points of the separator, which can lead to disadvantages in manufacturing costs and electrochemical performance[10,11].

In recent years, there have been intensive efforts to develop separators with better uniformity and wettability, thinner thickness, higher safety and more cost-effective. Many approaches have been reported to overcome the above disadvantages of commercial polyolefin separators. Among them, coating is an effective method to mitigate or avoid the thermal shrinkage of commercial polyolefin separators. Daeyong Yeon et al.[12] reported a flame-retardant composite separator by coating Al(OH)<sub>3</sub> and Mg(OH)<sub>2</sub> on PE separators with PVDF-HFP as binder and improved thermal stability and rate capability were observed. However, it was found that the Al(OH)<sub>3</sub> coated separator was electrochemically unstable during the cycling of batteries.

Grafting is another generally studied method to modify polyolefin separators. Xiaoming Zhu et al.[13] developed a ceramic (SiO<sub>2</sub>)-grafted PE separator using electron beam irradiation. A kind of silicon-oxygen crosslinked networks was grafted on PP separators through grafting polymerization and condensation reaction[14]. The resultant separators displayed much better thermal stability than untreated polyolefin separators without adverse effects on the performance of batteries.

As a versatile process to construct polymer nano-fibrous separators with high porosity, electrospinning process has gained

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a great deal of attention in the field of Li-ion battery separator. Electrospun nano-fibrous polyimide (PI) separators have been widely reported because of its high melting point [15–18]. Dezhi Wu et al. [16] fabricated a sandwich-like electrospun PI/PVDF/PI separator with an auto-shutdown capability above 170 °C and the modified separator showed superior cycling performance and rate capability compared to microporous PP separators. Wan Ye et al. [17] prepared a novel polyaniline-nanowires-coated polyamide nanofiber separator via electrospinning and in-situ polymerization and it was demonstrated that the resultant separator possessed higher thermal stability and better electrochemical performances compared to the commercial polyolefin separators. The applications of electrospun cellulose as battery separator were also explored due to its attractive properties, including renewability, low cost, specific structures, thermal stability, and so on [19,20]. A renewable and thermal-resistant cellulose-based separator was prepared by Guanglei Cui et al. using electrospinning technique and dip-coating process and the electrochemical performance of the cells using the proposed composite electrospun separator was enhanced [19].

Apart from the nano-fibrous nonwoven materials mentioned above, the feasibility of nonwoven fabrics used as Li-ion battery separators were widely explored, including wet-laid [21–31], spunbond [10,32–35] and meltblown [36,37] nonwoven materials, owing to their superior thermal properties, large pore size, high porosity, and cost competitiveness. Among these nonwoven fabrics, wet-laid nonwoven fabric was studied mostly because of its good homogeneity, sufficient mechanical strength and more choices in compositions including glass-fiber [23,25,29], aramid [24], PET [26,28] and cellulose [20–22,27,30,31]. As we know, the average pore size of wet-laid nonwoven fabrics is normally in the range of 5  $\mu\text{m}$  to 10  $\mu\text{m}$  by using fine fibers, which is insufficient to be used as Li-ion battery separators. Hence most studies focus on how to decrease the pore size by forming composite materials.

Sen Zhang et al. [25] fabricated a nano-composite polymer separator by coating nanoTiO<sub>2</sub>/PVDF-HFP onto both sides of glass-fiber wet-laid nonwoven fabric. The nanoTiO<sub>2</sub> used was grafted with PMMA, which contributed to its evenly disperse in PVDF-HFP solution. Improved properties such as thermal endurance (over 500 °C), porosity (58%), ionic conductivity (3.45 mS/cm) as well as interfacial compatibility to Li electrode were observed, leading to excellent rate and cycling properties. Wei Xiao et al. [26,28] coated NaA-type zeolite/PVDF-HFP and ZrO<sub>2</sub>/PVDF-HFP onto PET wet-laid nonwoven fabrics respectively, and the composite separators showed superior properties compared to commercial microporous polyolefin separators. A single ion polymer electrolyte composed of polymeric lithium tartaric acid borate salt (PLTB) and PVDF-HFP was coated on the surface of wet-laid cellulose nonwoven material via dip-coating process, and the resultant composite separator exhibited fascinating characteristics including higher ionic conductivity, good flame retardancy and superior thermal resistance [31].

Among nonwoven techniques, meltblown is efficient to produce fabrics with ultrafine fibers with diameter less than 5  $\mu\text{m}$ , allowing to produce thinner fabrics with lighter basic weight. Dezhi Wu et al. [36] prepared a composite PVDF/PET/PVDF separator with a sandwich-like structure by hot-pressing PVDF electrospun membranes on the surfaces of PET meltblown fabric. The composite separator showed excellent mechanical property, better wettability, higher thermal stability and excellent discharge capability compared to a commercial PP separator. Constituted with filaments, spunbond nonwoven fabrics possess high mechanical strength and can be used as the substrate of composite Li-ion battery separators. Xiaofei Li et al. [32] first grafted octafluoropentyl methacrylate (OFPMA) on the surface of PP nonwoven by plasma treatment, with the aim to improve the

nonwoven's adhesion with PVDF-HFP, and then coated SiO<sub>2</sub>/PVDF on the surface of PP nonwoven fabric. The composite separator using PP nonwoven fabric treated by plasma for 10 min exhibited the most satisfying performance, including improved mechanical property, electrolyte uptake, and ionic conductivity, leading to a superior C-rate performance and cycling performance.

As is demonstrated above, composite separators with nonwoven fabrics as substrate have great potential to replace the commercial polyolefin separators. Moreover, PVDF-HFP has been extensively studied and used to fabricate composite separators due to its high affinity to electrolyte, good thermal stability, high dielectric constant, and excellent chemical stability [38–41]. Hence, nonwoven fabric composited with PVDF-HFP is a promising candidate of separator for Li-ion battery. However, PVDF-HFP composite nonwoven separators were often fabricated via coating methods [10,42–44]. Pores of nonwoven fabrics were partly blocked by gel polymers, limiting the transmission of Li ions. At the same time, a rough surface sometimes will be formed, leading to inferior contact between the separator and electrodes.

To further improve the performance of composite nonwoven Li-ion battery separators, we demonstrated a composite nonwoven separator with a novel sandwich-like structure. A kind of porous PVDF-HFP membrane was made first by phase inversion process coated with a thin layer of SiO<sub>2</sub> particles, which is believed to increase ionic conductivity of the membrane [45,46]. SiO<sub>2</sub> was also added in the dope of PVDF-HFP membrane. Then a kind of nonwoven fabric dipped with PVDF-HFP solution was sandwiched between two pieces of PVDF-HFP membranes and hot pressed to fabricate the composite nonwoven separator. The morphology, wettability, thermal stability and electrochemical properties of the composite nonwoven-based separators were investigated as well.

## 2. Experimental

### 2.1. Materials

PVDF-HFP ( $M_w = 600,000$ , 12mol% HFP) was purchased from Solvay. SiO<sub>2</sub> particles with size of 100 nm and 15 nm were obtained from Jingrui New Material Inc. and Aladdin Industrial Inc., respectively. 1MLiPF<sub>6</sub> in DMC/EMC/EC/VC solution (DMC/EMC/EC/VC = 46.08/22.91/27.22/3.79 in volume) was purchased from Zhuhai Smoothway Electronic Materials Inc. Acetone was supplied by Wokai Chemical Technology Inc. Li(Ni<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>)O<sub>2</sub> was supplied by Xinxiang Tianli Energy Material Inc. A commercial PE separator (16  $\mu\text{m}$ ) was purchased from W-scope Inc. All chemicals were used without further purification.

### 2.2. Preparation of the composite nonwoven-based separator

It took three steps to prepare the composite nonwoven separator. Firstly, certain amounts of SiO<sub>2</sub> with size of 100 nm were added into acetone and stirred 2 hours, following a 30-minute ultrasonic vibration to form a 6 wt.% homogeneous suspension. Then SiO<sub>2</sub>/acetone suspension was coated on a piece of glass plate using a doctor blade with a gap of 10  $\mu\text{m}$ . After the evaporation of acetone, a thin layer of SiO<sub>2</sub> was formed on the surface of glass plate.

Secondly, PVDF-HFP/acetone solution with a series of concentrations (5 wt.%, 7 wt.% and 10 wt.%) were prepared by dissolving PVDF-HFP in acetone at 50 °C after stirring 4 hours. 5 wt.% deionized water was added slowly in order to induce the phase inversion in the later stage. Then SiO<sub>2</sub> particles with size of 15 nm were added to PVDF-HFP solutions with a PVDF-HFP/SiO<sub>2</sub> weight ratio of 10:1. Then the resulting solutions were coated on the glass plate with a layer of SiO<sub>2</sub> by using a doctor blade with a gap of 100, 70 and 50  $\mu\text{m}$ , respectively. Finally, the samples were dried at

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