Functional separator consisted of polyimide nonwoven fabrics and polyethylene coating layer for lithium-ion batteries

Chuan Shi, Peng Zhang, Shaohua Huang, Xinyi He, Pingting Yang, Dezhi Wu, Daoheng Sun, Jinbao Zhao

State Key Lab of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, PR China
School of Energy, Xiamen University, Xiamen 361102, PR China
School of Physics and Mechanical & Electrical Engineering, Xiamen University, Xiamen 361005, PR China

HIGHLIGHTS

- Nonwoven PI as structural support and PE particles as coating layer.
- PE–PI–S with a shutdown temperature range from 120°C to more than 200°C.
- Battery with PE–PI–S shows stable cycling and good rate performance.

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ABSTRACT

In this paper, a composite membrane with nonwoven polyimide (PI) membrane as structural support and polyethylene (PE) particles coating layer as a thermal shutdown layer, is fabricated as the separator for lithium-ion battery. Different from PI nonwoven membrane, the PE coating PI nonwoven composite membrane (PE–PI–S) not only shows excellent thermal shutdown function, similar to traditional multilayer PP/PE/PP separator, but also exhibits much higher thermal stability, better wettability to the polar electrolyte and lower internal resistance than the PP/PE/PP separator. The electrolyte uptake and ionic conductivity of PE–PI–S increase from 58%, 0.84 mS cm⁻¹ to 400%, 1.34 mS cm⁻¹, respectively. Furthermore, the thermal shutdown function of PE–PI–S can be controlled widely in the temperature range from 120°C to more than 200°C while the multilayer PP/PE/PP separator only with a shutdown temperature range from 130°C to 160°C. Lithium ion battery with PE–PI–S nonwoven separator also shows excellent stable cycling and good rate performance.

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1. Introduction

In most commercialized lithium-ion batteries, polyolefin porous membranes, specifically polyethylene (PE) and polypropylene (PP), have been used as separators to prevent the physical contact between the positive and negative electrodes while permitting free ionic transport within the cell [1,2]. Although such membranes offer some advantages such as excellent mechanical strength and chemical stability, they tend to exhibit large thermally induced dimensional shrinkage at high temperature [1,3] which could cause an electric shorting between the electrodes in cases of some inevitable occurrence of hazardous behaviors, such as electrical overcharging and high thermal impact. Resulted short circuit usually causes the thermal runaway of lithium-ion batteries (LIB), which could eventually lead to fire or explosion of the cells. A shutdown separator composed by multilayer polyolefin such as PP/PE/PP (such as Celgard 2340) is commonly used as a fail-safe device in commercial cells to solve the problem [1]. In the laminated multilayer PP/PE/PP separator, as shown in Fig. 1a, the high melting component PP serves as mechanical support while the low melting PE serves as shutting down agent. As the temperature of the battery cell approaches the melting point of PE (~130°C), the porosity in PE layer collapses, the ion conduction pathway is blocked thus the electrochemical reaction is terminated, however if the temperature...
continues to increase above the melting point of PP (~160 °C), the PP layers start to shrink and the separator could fail in separating the electrodes, thereby a potential internal shorting of the cell could occur. Even though such membranes offer some advantages as an excellent mechanical strength and chemical stability, but they can not function well as separator at higher temperature.

To improve the thermal safety of lithium ion battery, many efforts have been devoted to minimize the shrinkage of separator. Nonwoven membrane [4–16] have been widely studied as they exhibit excellent thermal stability, better wettability for the polar electrolyte and lower resistance. Batteries assembled with nonwoven separator usually show a higher capacity and rate capability. However, this type of separator exhibits several intrinsic disadvantages. Firstly, the ion conduction pathway cannot be cut off when the battery is exposed to high temperatures since nonwoven membrane is without the shutdown function. Secondly, there are certain amount of nano-sized conductive powders such as acetylene black using in the cathode and anode of LIBs. The small conductive powders, usually 40–50 nm in size, can easily enter the pores formed by electrospinning process with large or “giant” size and potentially migrate through the connected pores to the counter electrode, and resultantly cause self-charge and the soft-short circuit of the cell, which often happens in the failed cell. To overcome the disadvantages mentioned above, sandwiched-structured, such as Poly(vinilidenefluoride) (PVDF)/Poly(m-phenylene isophthalamide) (PMIA)/PVDF and Poly(phthalazinone ether sulfone ketone) PPESK/PVDF/PPESK nonwoven membrane [17,18] were designed. Similar to PP/PE/PP separator, the low-melting materials serve as the shutdown layers while the high-melting materials serve as the support layer. However, there is no direct evidence to prove that the ion conduction could be cut off with increased temperature, since no information of ion conduction change with increased temperature was provided. Another method is that PI nonwoven membrane was coated by inorganic/organic hybrids, such as Al2O3 and SiO2 [19–25], but those membranes are unattractive without shutdown function.

Poly(ethylene) (PE) microspheres provide thermal shutdown functionality when they were applied in lithium battery [26,27] has been reported previously. Poly(ethylene) (PE) microspheres coated on the anode or polylefin separator. In our work, a composite membrane with nonwoven PI as structural support and a PE layer as shutdown function was manufactured for the first time by an electrospinning method followed by a subsequent coating process. PI have been widely used [28–31] as the separator matrix or the coating material due to its excellent thermal stability, outstanding mechanical property, low thermal expansion coefficient and high inertness toward solvent and high radiation resistance. PI nonwoven with high thermal stability and high porosity as the supporting matrix exhibits little thermal shrinkage up to 200 °C, good wettability and low resistance toward the polar electrolyte. PE has already been successfully used as lithium ion battery separator component due to its inertness toward other lithium ion battery components and electrochemical reactions, and it also possesses the ability to block lithium ion conducting pathways at temperatures above 120 °C. Thus it is possible to fabricate a PE–PI–S separator that can provide the shutdown functionality when a temperature is above 120 °C and keep its dimensionality intact up to more than 200 °C, so that the thermal safety of the cell is highly enhanced.

Compared to a multilayer PP/PE/PP separator, the PE–PI–S separator exhibits better thermal stability, better wettability toward polar electrolyte and thus lower resistance. The electrolyte uptake and ionic conductivity of PE–PI–S are 400% and 1.34 mS cm−1 compared to 58% and 0.84 mS cm−1 of PP/PE/PP separator. Furthermore, even though PE–PI–S has similar shutdown temperature as PP/PE/PP, but its structural stability upon thermal agitation is much improved, thus the cell thermal safety is much enhanced. Coin cells with PE–PI–S as separator also shows excellent stable cycling and good rate performance.

2. Experiment

2.1. Fabrication of PI nonwoven membrane and PE–PI–S nonwoven membrane

PI and dimethylacetamide (DMAc) mixture (PI with a weight percentage of 20%) purchased from Hangzhou surmount science & technology (Hangzhou, China) with a vigorous mixing by magnetic stirring for 10 h. PI nonwoven porous membrane was fabricated by the electrospinning process with the result slurry. The setup for preparing the PI nonwoven membrane included a pump (Harvard, USA), syringe, high voltage source (Gamma, USA) and a copper collector placed on top of an X–Y motion stage (Googletech, Shenzhen, China). The anode of the high voltage source was connected to the conductive spinneret while the ground collector was connected to the cathode. The flow rate of the PI solution was 100 μL h−1 and the electrospinning process was conducted under an applied bias of 10 kV with 10 cm of spinneret-to-collector distance. The collector then moved back and forth at a speed of 40 cm min−1 in the X-axial direction with a moving displacement of 12 cm and moved intermittently in the Y-axial direction (40 μm when the collector reached one end of the X-directional scanning range) for better distribution and uniformity of nano-fibers.

PE miniemulsion, purchased from Michelman with a mean
diameter of 50 nm, was granulated again by spray-dried in the machine (Buchi, Switzerland). The treated particles were used in the next experiments.

The slurry for PE was prepared by mixing PE particle, SBR and CMC (Guangzhou Songbai Chemical, China) into a water/ethanol (5 ml: 5 ml) mixed solvent, the weight of PE/SBR/CMC was fixed at 0.90 g/0.06 g/0.04 g. After ultrasonically dispersed for 10 min, the slurry was further subjected to vigorous mixing by magnetic stirring for 10 h. The coating slurry was applied onto one side of the PI nonwoven membrane with a scraper. After the coating, the prepared separator was dried under vacuum at 60 °C for 6 h to remove the solvent.

2.2. Electrode preparation and cell assembly

The battery performance of the material was tested using coin cells. Metal Li was used as the anode. The cathode had a composition of 90 wt. % LiMn2O4 (Qingdao xinzheng material co., Ltd, China); 5 wt. % Super-P, 5 wt. % PVDF. The N-methyl pyrrolidine (NMP)-based cathode slurry was coated on a 15 μm thickness aluminum foil and the electrode was dried overnight at 80 °C in a vacuum drying oven. For comparison, three different separators were tested: PP/PE/PP as baseline, PI nonwoven, and PE–PI–S nonwoven composite. The coin cell was injected the same weight of electrolyte. All cells were assembled in a glove box (Mbraun, Germany) filled with argon gas.

2.3. Characterization of the membranes

The surface and cross-section morphologies of the PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane were investigated using a field emissions scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). The thermal shrinkage of the membranes were determined by measuring the dimensional change (area based, cycle with 1.85 cm diameter) after being subjected to heat treatment at various temperatures for 1 h and the shrinkage can be computed as the following equation:

\[ \text{shrinkage (\%)} = \frac{S_0 - S}{S_0} \times 100\% \]

where \( S_0 \) and \( S \) stand for the area of separator before and after heat treated.

The contact angle measurement of the PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane were carried out using a commercial drop shape analysis system (Powereach JC2000C1, Shanghai Zhongchen Digital Technique Equipment Co. Ltd., China) to analyze the wettability of the electrolyte.

The porosity of the membrane was computed according to the following equation:

\[ P(\%) = \frac{M_{\text{BuOH}}}{\rho_{\text{BuOH}} \times (M_{\text{BuOH}}/\rho_{\text{BuOH}} + M_{m}/\rho_{P})} \times 100\% \]

where \( M_{m} \) and \( M_{\text{BuOH}} \) represent the mass of membrane before and after absorbed n-butanol, respectively, while \( \rho_{\text{BuOH}} \) and \( \rho_{P} \) represent the densities of n-butanol and polymer, respectively.

The electrolyte uptake was computed according to the following equation:

\[ \text{Uptake} \% = \frac{W - W_0}{W_0} \times 100\% \]

where \( W_0 \) is the net weight of membrane, and \( W \) is the weight of the membrane after absorbing the liquid electrolyte.

The ionic conductivities of PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane with electrolyte were measured by sandwiching the membrane between two stainless steel electrodes. Impedance data were obtained with electrochemical workstation (Solartron, SI-1260, England) over a

Fig. 2. (a) The SEM of PE particles after granulation again by spraying drying machine (b) surface of PP/PE/PP separator (c) surface of PI nonwoven membrane. (d) surface of PE–PI–S nonwoven membrane.
frequency range of 1 kHz–100 kHz. The differential scanning calorimetry (DSC) (STA 449 F3 Jupiter Netzsch) was used to measure the thermal stability of membrane from 30 °C to 200 °C with heating rate of 5 °C min⁻¹. The charge and discharge cycling tests of the cells were measured at 0.5C with battery test equipment (LAND-V34, Land Electronic, China). Cells were charged to 4.2 V and discharged to 3 V at current rates of 0.1C, 0.2C, 0.5C, 1.0C and 2.0C for the measured of rate capacity.

3. Results and discussions

The SEM of granulated PE particles with a mean average of 1–2 μm is shown in Fig. 2a. The SEM of the top surface of PP/PE/PP separator, PI nonwoven membrane and PE coating PI nonwoven membrane are shown in Fig. 2b, c, d respectively. The PP/PE/PP separator shows a typical morphology of dry process with a uniformly elliptic submicron pore structure. The long axis of the pore was 100–200 nm and the short axis is about 50 nm. The PI nonwoven membrane made of nano-fibers was shown in Fig. 2c. The fibers exhibited uniform diameters and there were no observable beads on the fibers. These long nano-fibers with a diameter of 100–200 nm forms the highly porous network structure. The highly interconnected micro-porous structure is essential in absorbing more electrolyte while allow lithium ions to transport, thus resulting in high ionic conductivity. However, these “giant” irregularly pores formed between the PI nano-fibers could potentially lead to self-discharge or uneven current distribution. Compared with the PI nonwoven membrane with large-sized pores, the PE–PI–S nonwoven membrane, shown in Fig. 2d, is more desired. The sizes of the pores on the PE–PI–S membrane surface were remarkably reduced with PE particle homogeneously coated onto the surface of porous network structure while maintains the same PI network structure with highly tortuous pores.

The basic function of a separator is to prevent physical contact between the positive and negative electrodes while enable fast ionic transport. Thus, the separators should be chemically and mechanically stable inside the cell at charged and discharged states and at elevated temperatures, otherwise, they will either cause unwanted side reactions to deteriorate cell performance or will not separate the anode and cathode, causing a potential thermal runaway, even combustion or explosion. In order to investigate the thermal-resistant characteristics of pristine PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane, thermal shrinkage behavior is studied by measuring the dimensional change (area-based) after storing the membranes at 110 °C–200 °C for 30 min. Fig. 3 shows the thermal shrinkage of pristine PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane before and after the thermal shock. It can be seen from Fig. 3a that the PP/PE/PP separator is easy to lose the dimensional stability after exposure to high temperatures of over 115 °C. The thermal shrinkage of PP/PE/PP separator suffered a fast increase near 130 °C and after 160 °C, corresponding to the melting of PE and PP respectively. PI nonwoven separator and PE–PI–S separator almost suffered no thermal shrinkage in the temperature range of 110 °C–200 °C. The result is much owed to the excellent thermal stability of PI nano-fiber. It can be seen from Fig. 3b that the PP/PE/PP membrane exhibits a large shrinkage and its color changes from white to transparent at 140 °C, and it cannot be measured at 200 °C as it completely melts and cannot be measured totally. On the other hand, the PI and PE–PI–S nonwoven membranes show neither dimensional shrinkage nor color change. Thus, it can be expected that the thermal stability of the lithium-ion batteries will be significantly improved when PI nonwoven membrane and PE–PI–S nonwoven membrane are applied as battery separators.

The SEM images of surface of PP/PE/PP separator and PE–PI–S nonwoven membrane after heat treatment at 140 °C for 30 min were shown in Fig. 4a and Fig. 4b. From these figures it can be found that both separators form a dense layer since the pores in PP and PE layers collapse in the case of PP/PE/PP separator and the pores of PI nonwoven membrane were blocked by the melted PE layer at 140 °C.

To verify our hypothesis that at elevated temperature all the pores in PP/PE/PP collapse while in PE–PI–S composite separator the pores are blocked by melted PE, SEM images of the cross-sections of PP/PE/PP separator and PE–PI–S nonwoven membrane before and after heat treatment at 140 °C for 30 min was taken and shown in Fig. 5. The cross-section of PP/PE/PP separator before and after hot treatment is shown in Fig. 5a and b. From these images it is indeed that all the pores in the PP and PE layers in PP/PE/PP separator collapsed to form a dense layer after heat treatment. The cross-section of PE–PI–S nonwoven membrane before and after hot treatment is shown in Fig. 5c and d. The thickness of the PI nonwoven membrane and PE coating layer is about 20 μm and 6 μm. After heat treating at 140 °C for 30 min, the pores in the PE layer totally disappeared and the top portion of PI nonwoven membrane was plugged up by the melting PE materials. In order to further improve that the holes in the surfaces of PI nonwoven membrane was plug up by the melting PE materials, porosity of PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane at gradient temperature (b) Optical photographs of PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane the annealing treatments for 0.5 h.
PE/PP separator, PI nonwoven and PE–PI–S nonwoven membrane before and after hot treatment were measured and shown in Table 1. The PI nonwoven membrane almost maintains the original porosity after hot treatment, while the PP/PE/PP turned into a dense layer after hot treatment. The porosity of PE–PI–S decreased from 60% to 38.2% after hot treatment at 140 °C for 0.5 h as a result of the holes in the surfaces layer of PI nonwoven membrane was plug up by the melting PE materials after hot treating which is thought could cut off the ion conduction of PI nonwoven membrane.

The wettability of the separator plays an important role in the battery performance due to the ability of separator to effectively retain the electrolyte solution and facilitate ion transport between electrodes. The contact angle of the electrolyte on the separator is one of the indicators for the wettability of the separator. The contact angle of PI nonwoven membrane and PE–PI–S nonwoven membrane decreases more rapidly than that of the PP/PE/PP membrane during the dynamic process. As show in Fig. 6, the contact angle for PP/PE/PP separator was measured as 35.0° after 5 s. The contact angle significantly decreased to 0° for PI nonwoven membrane and PE–PI–S nonwoven membrane after the same contact time with the electrolyte, which indicates a significant increase in the wettability of the membranes with the electrolyte. The lower contact angle of the PE–PI–S is attributed to its porous structure formed by the micron sized PE particles. The porous structure is different from that in the traditional porous PP/PE/PP membrane and is expected to play a key role in improving the electrolyte wettability.

The electrolyte uptake is an important indicator for the application of the separator. The electrolyte uptake and the ionic conductivity of a series of membranes were measured and are summarized in Table 1. The electrolyte uptake of PP/PE/PP separator, PI nonwoven membrane and PE–PI–S nonwoven membrane are 54%, 433% and 400%, respectively. The electrolyte uptake capacity of PI nonwoven membrane and PE–PI–S nonwoven membrane is almost eight times and seven times higher than that of the

![Fig. 4.](image1) (a) Surface SEM of PP/PE/PP separator after hot treatment at 140 °C for 0.5 h (b) surface of PE–PI–S nonwoven membrane after hot treatment at 140 °C for 0.5 h.

![Fig. 5.](image2) (a) Cross-section of PP/PE/PP separator before hot treatment (b) cross-section of PP/PE/PP separator after hot treatment at 140 °C for 0.5 h (c) cross-section of PE–PI–S nonwoven membrane before hot treatment (d) cross-section of PE–PI–S nonwoven membrane after hot treatment at 140 °C for 0.5 h.
PE separator. This can be explained by the fact that PI or PE–PI–S has higher degree of porosity and higher polarity. The electrolyte uptake capacity of PE–PI–S nonwoven membrane is a little lower than PI nonwoven as a result of PE particles coating layer, but still much higher than PP/PE/PP separator. Separator with high electrolyte uptake is expected to improve the ionic conductivity and the battery performance.

The ionic conductivities of PP/PE/PP membrane, PI nonwoven membrane and PE–PI–S nonwoven membrane after being soaked in an electrolyte solution at 30 °C is 0.84 mS cm⁻¹, 2.46 mS cm⁻¹ and 1.34 mS cm⁻¹, respectively (Table 1). The ionic conductivity of PE–PI–S is lower than that of PI nonwoven membrane but higher than that of PE membrane. From the ionic conductivity and wettability data, it could be concluded that the polar and highly porous PI nano-fiber nonwoven is beneficial for high ionic conductivity, and the composite separator even with less conducting PE coating layer can still be a much better separator compared to PP/PE/PP.

The shutdown behavior of a separator can be determined by electrochemical impedance measurement while heating the separator (saturated with electrolyte) to high temperatures as shown in Fig. 7. The changes of the impedance with the temperature were shown in Fig. 7a. From the figure we can find that the PP/PE/PP separators exhibited a larger increase in impedance at a temperature of about 130 °C that effectively stopped ionic transport between the electrodes. This was caused by the melted PE material at the middle layer of the separator blocking the hole of the PP layer. However, the impedance of PP/PE/PP separators exhibit a sharp decline to almost 0 Ω at a temperature of about 160 °C which indicates that the melted PP (~160 °C) shrinks and loses mechanical integrity thus can no longer serve as separator to separate cathode and anode and an electrical short circuiting is unavoidable. From the DSC profiles shown in Fig. 7b we observed that the PP/PE/PP had two endothermic peaks at 130 °C and 160 °C, respectively, which were attributed to the melting of the PE and PP materials. The DSC profiles agreed well with the above impedance increase and drop of the PP/PE/PP separator. The greater the mechanical integrity of the separator above the PE melting temperature, the greater the safety the separator can provide. The PE–PI–S nonwoven membrane exhibits a large increase in impedance at the start of temperature of about 120 °C and the resistance still maintains at high values even when the temperature is above 200 °C. The impedance change of PE–PI–S nonwoven membrane indicates that PE–PI–S nonwoven membrane can stand high temperature without dimensional change. The DSC profiles of PE–PI–S shown in Fig. 7b only exhibits an endothermic peak at about 120 °C with no other peak observed which is consistent with the facts above. However, this impedance drop of the PE–PI–S nonwoven

Table 1: Physical properties.

<table>
<thead>
<tr>
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<th>PP/PE/PP separator</th>
<th>PI membrane</th>
<th>PE–PI–S membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness μm</td>
<td>40</td>
<td>20</td>
<td>26</td>
</tr>
<tr>
<td>Density g cm⁻³</td>
<td>0.51</td>
<td>0.27</td>
<td>0.31</td>
</tr>
<tr>
<td>Porosity %</td>
<td>43.3</td>
<td>70.1</td>
<td>60.0</td>
</tr>
<tr>
<td>Porosity after hot treatment %</td>
<td>~0%</td>
<td>70.0</td>
<td>38.2</td>
</tr>
<tr>
<td>Electrolyte uptake %</td>
<td>54</td>
<td>433</td>
<td>400</td>
</tr>
<tr>
<td>Ionic conductivity ms cm⁻¹</td>
<td>0.84</td>
<td>2.46</td>
<td>1.34</td>
</tr>
</tbody>
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![Fig. 6. The contact angle tests of the three membranes: (a) the PP/PE/PP separator (b) the PI nonwoven membrane (c) the PE–PI–S separator.](image-url)
membrane at 172 °C which may be due to the facts that PE becomes a fluid at this temperature and there is not enough PE to block the "giant" PI pores. Furthermore, the start temperature of thermal shutdown function can be controlled widely by the application of different molecular weight polyethylene and different polyolefin materials. The further work is underway.

**Fig. 7.** (a) The impedance change to high temperatures with a heating-rate 1 °C min⁻¹ of the PP/PE/PP separator and PE–PI–S nonwoven membrane (b) the DSC of PI, PP/PE/PP and PE–PI–S membrane.

**4. Conclusion**

In conclusion, compared with the PP/PE/PP separator, PE–PI–S nonwoven membrane exhibits excellent thermal stability, better wettability with the polar electrolyte, lower resistance and the battery assembled with this membrane shows higher capacity and rate capability. More importantly, PE–PI–S nonwoven membrane can provide the shutdown function in a temperature range from 120 °C to more than 200 °C. With such advantages mentioned above, the PE–PI–S is suitable for applications in high-safety/high-rate lithium-ion batteries.
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