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Improvement of meltdown temperature of lithium-ion battery separator using electrospun polyethersulfone membranes

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ABSTRACT

Polyethersulfone (PES) electrospun nanofibrous membranes have been prepared and deposited on both sides of a microporous polyethylene (PE) substrate to fabricate a nanocomposite separator, which exhibits a high meltdown temperature (MDT) to prevent the thermal runaway within the battery under the condition of overcharging or abuse. To improve adhesion to electrospun PES nanofibrous membranes, the PE substrate with low surface energy and hydrophobic nature was etched with chromic acid and characterized with atomic force microscopy (AFM) and infrared spectroscopy (FTIR) techniques as well as the water contact angle test. Compared to the original film, the modified PE substrate showed a nearly 10-times increase in adhesive strength to the electrospun PES membrane. The morphology of the electrospun PES membrane, controlled by different electrospinning flow rates, was also demonstrated to have a substantial impact on adhesion, where a 5-fold increase of the adhesive strength was observed when the flow rate increased from 20 μL/min to 60 μL/min. The composite PES/PE/PES separator, structured as a PE substrate sandwiched in 2 electrospun PES membranes, maintained the low shutdown temperature (SDT) of 131 °C but achieved a significantly higher MDT of 221 °C. Furthermore, the high porosity of the electrospun PES membrane ensured that the air permeability of the separator was not sacrificed when compared with the original PE separator.

1. Introduction

Lithium-ion batteries (LIBs), owing to their advantages, such as better self-discharge performance, longer cycle life, higher energy density, and higher operational voltage over the NiCd and NiMH systems [1], have been used in over 90% of cell phones, laptops, camcorders, and many hybrid electric vehicles (HEVs) and electric vehicles (EVs) [2–6]. A lithium-ion battery consists of a metal oxide (e.g., $LiCoO_2$) positive electrode and a graphite negative electrode where a porous separator film is placed between the 2 electrodes and is immersed in the ionically conductive electrolyte [7–9]. The separator film plays an important role in the lithium-ion battery, which allows the ionic flow and keeps the positive and negative electrodes apart to prevent short circuits within the battery. The pore size of the film in the submicron range (<1 μm) has been shown to be small enough to prevent dentritic lithium going through [5,10].

A microporous polyethylene (PE) separator film, due to its low melting point at around 135 °C, provides a safety feature to prevent thermal runaway reactions in the battery. When the cell temperature reaches the shutdown temperature, slightly lower than the melting point of PE, the separator works as a thermal fuse by shutting down the pores and thus prevents ionic transport and cell reaction. However, if the temperature is further elevated above the melting point of the separator, the separator is highly likely to undergo a complete meltdown and lose its mechanical integrity, which results in the contact of the electrodes and direct chemical reaction, leading to severe damage to the battery [11–13]. An ideal separator should possess a low SDT and a high MDT, and therefore could provide a greater safety margin to the battery. To enhance the MDT of the PE separator, Celgard, LLC developed the PP/PE bi-layers and PP/PE/PP tri-layers combing the low melting temperature of PE and the high melting temperature of polypropylene (PP), with the

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MDT being increased to around 180 °C [14]. Chung et al. conducted the PE substrate coating with various amounts of ethylene glycol dimethacrylate (DEGDMA) by radical polymerization in ethanol solution. The MDT of the coated PE separator was increased to 155 °C [15]. They also coated the PE substrate with nanocomposites composed of DEGDMA polymer and silica nanoparticles, which increased the MDT to 170 °C. However, this coating approach decreased the porosity of the membrane and therefore reduced the battery performance [16]. Electrospun nanofibrous membrane with high porosity of 70%–80%, and adjustable pore size falling in the range of microns and submicrons [17,18], has also been demonstrated to be capable for use as a LIB separator; however, the electrospun membrane does not provide the shutdown feature [19,20]. It should be ideal to make a composite membrane, which combines the advantages of the PE separator (i.e., shutdown feature) and the electrospun membrane.

PES is the material that exhibited great chemical and mechanical stability and, more importantly, excellent heat resistance (with a T_g ~ 220 °C based on different sources) [21,22]. Unfortunately, the adhesion of PE to other materials is usually poor due to its low surface tension (30–31 dyn/cm), hydrophobic, and chemically inert properties [23,24]. Both physical and chemical methods can be used to improve surface adhesion. The physical method generally involves mechanical abrasion to generate more surface roughness, therefore enhancing mechanical interlocking with the adhesive [25,26]. Meanwhile, a wide variety of surface chemical modification methods such as chemical etching [27–31], flame treatment [32], plasma treatment [29], and UV exposure [33] have also been reported to introduce polar functional groups onto the surface and to increase the surface tension.

In this work, a nanocomposite separator film was prepared by depositing the electrospun PES membrane directly on both sides of a porous PE substrate, resulting in a sandwiched structure. A chemical modification method using chromic acid was applied on PE substrate, with the modification degree controlled by the acid treatment time, to improve the adhesive strength between PE and PES. The adhesion was also optimized by controlling the morphology of the electrospun PES membranes through the feeding rate of polymer solution during the electrospinning process. It was expected that the meltdown temperature would be greatly improved above that of the commercial PP/PE/PP film, while the new sandwiched structure could still keep the low shutdown temperature of the PE substrate. Also, due to the high porosity of the electrospun PES membrane, the porosity of the PE substrate was not likely to be reduced and the performance of the separator would not be sacrificed. The preliminary tests on the separator film properties of the PES/PE/PES composite membrane were carried out at Exxon Mobil Chemical Corp.

2. Experimental

2.1. Materials

Poly(ethersulfone) (PES) with a weight-average molecular weight (M_w) of 63,000 g/mol was purchased from Solvay Advanced Polymers. Dimethylformamide (DMF, 99.9%), potassium dichromate, and sulfuric acid (95.0–98.0%) were purchased from Sigma Aldrich. PES powder was dried in vacuum at 120 °C for 6 h, and DMF was dried over molecular sieve (3 Å) before use. The polyethylene lithium ion separator film (E25MMS) with an average thickness of 25 μm was provided by the Exxon Mobil Chemical Corp.

2.2. Preparation of electrospinning solution

A certain amount of PES powder was dissolved in the solvent of DMF and the solution was stirred at 90 °C for 2 days to make the electrospinning solution with the concentration of 28 wt% [34,35].

2.3. PE substrate treatment

The polyethylene lithium ion separator film (E25MMS) was chosen as the base substrate. This PE substrate was first immersed in ethanol followed by washing with de-ionic (DI) water several times to remove surface contaminants. The chromic acid solution was prepared based on the literature [31], where a weight ratio of K_2CrO_7:H_2O:H_2SO_4 = 7:12:150 was employed. The PE substrate was immersed in the chromic acid solution at room temperature for 0 s, 10 s, 30 s, 60 s, 120 s, and 240 s, respectively; then, it was washed in running distilled water overnight and dried in vacuum before use.

2.4. Electrospinning of PES membrane

A typical custom-built electrospinning setup was used to fabricate PES nanofibrous membrane. The detailed description of the equipment can be found in the literature [18]. The treated PE substrate with chromic acid solution was taped on the aluminum foil wrapped on a rotating drum (diameter: 10 cm, rotating speed: 300 rpm), and the spinneret-to-collector distance was set at 10.5 cm with the applied voltage of 12 kV. A stepping motor was used to control the oscillatory translational motion of the spinneret in order to achieve the electrospun membrane with uniform thickness. Different flow rates of PES polymer solution, 20 μL/min, 40 μL/min, 60 μL/min, and 80 μL/min were employed in the electrospinning process. The electrospinning performance was operated in a closed chamber, with a temperature of 26 ± 1 °C and a relative humidity of 40± 2% monitored by a temperature and humidity meter (catalog number: 11-661-19, Fisher Scientific).

2.5. Characterizations of the chemically treated PE surface

The surface topology of the PE substrates before and after treatment was characterized using an atomic force microscope (AFM) (Dimension 3000, VEECO, Plainview, NY) equipped with version 5.12r5 NanoScope III Software. The chemical change of the surface produced by the chromic acid etching was characterized using Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR) accessory (Nicolet iS10 spectrophotometer, Thermo Scientific, Inc.). Each sample was scanned 16 times in the wavenumber range of 4000–650 cm^{-1}. The surface hydrophobicity was determined with a water contact angle goniometry (CAM200 Optical Contact Angle Meter, KSV Instruments, Ltd.), where 10 μL of Milli-Q water was used as a probe liquid and three different spots were tested for each sample.

2.6. Characterizations of electrospun PES membrane and adhesion strength measurements

The electrospun PES membrane was deposited on one side of the treated PE substrate only in the following tests. Scanning electron microscopy (SEM, LEO 1550) was employed to observe the morphology of the electrospun PES membrane after platinum-sputter coating, where the average nanofiber diameter and standard deviation can be figured out using Leica software (http://dell.chem.sunysb.edu). By measuring the total thickness of the PES/PE membrane with a digital micrometer, the thickness of the PES electrospun layer can be calculated by the difference of the total PES/PE membrane and that of the PE substrate. The porosity of the PES electrospun layer was calculated based on the gravimetric method [36], where the PES bulk density of 1.37 g/cm^3 has been used.