



Electrochemical performance of a thermally rearranged polybenzoxazole nanocomposite membrane as a separator for lithium-ion batteries at elevated temperature



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HIGHLIGHTS

- TR-PBO membranes with high thermal and electrochemical stability were prepared.
- The structure of TR-PBO membranes has an effect on the electrochemical performance.
- TR-PBO membranes show excellent Li-ion cell performance at high operating temperature.
- Sea-squirt structured nanoparticles help the membrane wettability and ionic transport.

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ABSTRACT

Shape-tunable hydroxyl copolyimide (HPI) nanoparticles are fabricated by a re-precipitation method and are coated onto electrospun HPI membranes, followed by heat treatment to prepare thermally rearranged polybenzoxazole (TR-PBO) composite membranes. The morphology of HPI nanoparticles consisted of sphere and sea-squirt structures, which is controlled by changing the concentration of the stabilizer. The morphological characteristics of TR-PBO nanoparticles convert from HPI nanoparticles by heat treatment and their composite membranes is confirmed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy (ATR-IR), thermogravimetric analysis (TGA) analysis, and contact angle measurements. TGA and DSC measurements confirm the excellent thermal stability compared to Celgard, a commercial PP separator for lithium-ion batteries (LIBs). Further, TR-PBO nano-composite membranes used in coin-cell type LIBs as a separator show excellent high power density performance as compared to Celgard. This is due to the fact that sea-squirt structured nanoparticles have better electrochemical properties than sphere structured nanoparticles at high temperature.

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1. Introduction

Lithium-ion batteries (LIBs) with high electrochemical performance are the most common choice of power source for portable

electronic devices such as cellular phones, notebooks, and cameras [1–3]. In the future, LIBs must be safe to use and have an increased cell capacity, as required for large, high current density batteries for rapidly charge/discharge of electric vehicles and energy storage systems. The safety of a battery is closely related to the thermal stability of the separator and the flammability of the liquid electrolyte; this is because an explosion can result from the thermal shrinkage of the separator and the subsequent ignition of the flammable liquid electrolyte under demanding conditions [4,5]. Therefore, the separator plays an important role in regulating cell kinetics, allowing ionic flow, blocking a short circuit between two electrodes, and acting as a safety device. The separators most

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generally used are based on polyolefins such as polyethylene (PE) and polypropylene (PP), and these show good performance due to their mechanical strength and chemical stability. However, they are unfavorable for use in next generation batteries due to their relatively low thermal stability and poor electrolyte wettability [6–8].

Organic or inorganic particles coated with polyolefin membranes have been investigated by some researchers to improve the thermal stability of the separator. Choi et al. prepared an Al₂O₃ powder coated PE membrane with a hydrophilic poly(lithium 4-styrenesulfonate) binder [9]. These separators exhibited enhanced thermal stability and a 3.8% shrinkage ratio at 105 °C, thereby largely retaining their initial dimensions. Preparation of polyimide-coated PE membranes by a simple dipping method was reported by Song et al. [10]. They found that the polyimide coating was very effective in suppressing thermal shrinkage without sacrificing its inherent battery performance. The thermal shrinkage ratio for the bare PE membrane was 83.3% after storage at 140 °C for 30 min, while that for polyimide-coated PE membranes decreased markedly to 10%. Another approach is using a nonwoven separator such as polyethylene terephthalate (PET) [11,12], poly(phthalazinone ether sulfone ketone) (PPESK) [13], polyimide (PI) [14,15], and thermally rearranged polybenzoxazole (TR-PBO) [16–26] membranes by an electrospinning method to develop thermally stable separators. Among these, thermally rearranged polybenzoxazoles (TR-PBOs) have proved to be promising materials for gas separation membranes due to their inherent ultra-pores, which induce both extraordinary permeability and selectivity [16–26]. Furthermore, in our previous study, we have developed the first TR-PBO LIB separators that show excellent thermal and dimensional stability and low cell resistance [27].

In this study, to prepare LIB separators with excellent electrochemical properties, we first made HPI nanoparticles with sphere and sea-squirt structures that were subsequently coated on an electrospun HPI nonwoven membrane. Then, the HPI composite membranes were converted into TR-PBO composite membranes. It is our aim to tune the shape of HPI and TR-PBO nanoparticles under controlled conditions and to investigate particle formation mechanisms. The ultimate goal of this study is to determine the relationship between the particle shape and cell performance in TR-PBO composite membranes as a potential separator for LIBs. TR-PBO membrane separators were compared with Celgard® 2400 in terms of electrochemical performance.

2. Experimental

2.1. Materials

To synthesize the hydroxyl copolyimide, three monomers were used: 4,4'-oxydiphthalic anhydride (ODPA, Shanghai Resin Factory Co. Ltd., China), 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB, Central Glass Co. Ltd., Japan), and 4,4'-oxydianiline (ODA, Central Glass Co. Ltd., Japan). N-Methyl-2-pyrrolidinone (NMP, Aldrich Chemical Co., Milwaukee, WI, USA) and o-xylene were used as solvents for polymer synthesis. For particle production, NMP was used as a solvent, while methanol, ethanol, and isopropanol (Sigma–Aldrich Corp., St. Louis, MO, USA), and deionized water (DI water) were used as non-solvents. Poly(vinyl alcohol) (PVA, average molecular weight 85,000) and poly(vinyl pyrrolidone) (PVP, average molecular weight 40,000) were also purchased from Sigma–Aldrich.

2.2. Hydroxy copolyimide (HPI) synthesis

Hydroxypolyamic acid (HPAA) was synthesized by an azeotropic imidization method as described in the literature [20]. Following the azeotropic imidization, the HPAA solution becomes an HPI

solution. Then, 60 ml of o-xylene was poured into the HPAA solution while the temperature was maintained between 160 and 180 °C for 6 h to fully imidize the amic acid groups into imide groups. After removing the eliminated water, the solution became a viscous, brown HPI solution. The solution was precipitated in a 3:1 water:methanol solution by using a mechanical mixer to effectively remove solvents. After washing the precipitated HPI powder overnight, a 3:1 water:methanol solution was again added followed by stirring 4 h. Subsequently, the solution was washed with deionized several times. Finally, the HPI powder was obtained and was vacuum dried at 150 °C for 12 h. Average molecular weights (Mw) of two batches of the synthesized polymer were measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF), and were 250,000 and 200,000.

2.3. Polymer nanoparticle fabrication

HPI nanoparticles were prepared by the re-precipitation method, as described in the literature [28]. HPI powders were dispersed into NMP at a concentration of 2 wt% with mechanical stirring. After dissolving in NMP, the HPI solution was filtered by using a 0.5- μ m PTFE syringe filter to remove any impurities. To prepare nanoparticles using stabilizers, two selected stabilizers, PVP and PVA, were added into the prepared solution with the same weight content of polymers. Then, a PVA or PVP solution was inserted into the polymer solution at a rate of 0.05 ml/min using a syringe pump (LB-200, Longer pump, China) in a four neck round bottom flask with no purge gas, which was pre-heated to 70 °C by an oil bath with mechanical stirring at 300 rpm. Depending on the total volume of the final solution, additional stirring was conducted. After the nanoparticles were fully prepared and stabilized, the flask was quenched with ice water to prevent any aggregation of nanoparticles. The particle solution was filtered with a pressurized paper filter and was centrifuged to wash off the residual using a 3:1 ratio of ethanol and DI. The particles were obtained by freeze drying at 0 °C for 30 h or more.

2.4. Preparation of electrospun HPI membrane

HPI powders were dissolved into dimethyl acetamide (DMAc, Aldrich Chemical Co. Milwaukee, WI, USA) in 8 wt% solution. A single nozzle system with an automated syringe pump (LB-200, Longer pump, China) was used to fabricate the electrospun HPI membrane. A rotating drum, with a diameter of 12 cm, was used as a collector, and was covered with polyethylene terephthalate (PET) as a backing material (BM), and was rotating at a speed of 10 rpm. The tip-to-collector distance was 15 cm. A syringe (Normject) with a nozzle (diameter of 6 μ m) was attached. Furthermore, the syringe was attached to an ES-robot (Nano NC, Korea), which moves in the x-direction in a range of 45–230 mm at a speed of 100 mm/min. The HPI solution was poured into the syringe and was directly electrospun at a speed of 0.5 ml/min to the collector for a total volume of 8 ml. During the injection, 10 kV and –4 kV were applied to the needle and the collector, respectively. After the electrospinning process, the electrospun HPI membrane was dried for 2 h at room temperature, and then was detached from PET BM. The membrane was then pressed at 130 °C using a pressure of 150 kgf/cm² to form the final electrospun membrane with a thickness of 18–20 μ m.

2.5. Fabrication of TR-PBO nano-composite membrane

The preformed HPI nanoparticles and nano-composite membranes were thermally rearranged into polybenzoxazole as follows. First, the temperature was increased by ramping at 10 °C/min to

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