



Ether modified poly(ether ether ketone) nonwoven membrane with excellent wettability and stability as a lithium ion battery separator



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HIGHLIGHTS

- Ether modified PEEK nonwoven membrane was exploited as LIB separator.
- The membrane keeps stable in various of solvents, even in concentrated H₂SO₄.
- The membrane is greatly wettable, reflected by the contact angle of 0°.
- The membrane shows no shrinkage after being treated at 180 °C for 12 h in air.
- The LIB equipped with the membrane shows elevated rate and cycling performance.

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ABSTRACT

In this study, poly(ether ether ketone) is first chloromethylated to improve the solubility and is later used for nonwoven membrane fabrication by electrospinning. Finally, the chloromethyl group was converted to the ethyl ether group and dibenzyl ether group in a hot alkaline solution. The abundant polar groups endow the membrane with excellent wettability, reducing the contact angle to 0°. The polymer matrix is crosslinked by dibenzyl ether group, endowing the membrane with excellent stability (insolubility in many solvents, and ultra-low swelling in the electrolyte at 80 °C) and good anti-shrinkage property (0% at 180 °C). The electrospinning-fabricated membrane remains stable until 4.812 V (vs. Li⁺/Li), meeting the requirement for use in lithium ion batteries. The interwoven structure of the nonwoven membrane effectively gives rise to the high electrolyte uptake of 215.8%. The ionic conductivity of the electrolyte-swelled electrospinning-fabricated membrane is 51% higher than that of the electrolyte-swelled Celgard membrane. As a result, the lithium ion battery with this nonwoven membrane exhibits an enhanced rate performance (up to 42.5% higher than the lithium ion battery with a PP separator) and satisfactory cycling performance.

1. Introduction

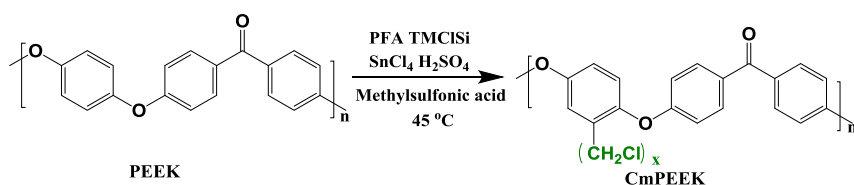
In recent decades, lithium ion batteries (LIBs) have been one of the most popular secondary power sources due to such advantages as high energy density, long life and portability [1–4]. The separator is an important LIB component that is sandwiched by the anode and the cathode and that plays the dual role of 1) preventing the short circuit of LIB by physically dividing the electrodes and 2) allowing the transport of lithium ion between the electrodes with the help of the electrolyte [5–7]. An ideal separator should be highly porous and wettable to obtain a low internal resistance of the LIB and a high electrochemical

performance. Meanwhile, it should be mechanically, thermally and chemically robust over the entire range of LIB operating conditions to ensure operational safety [6,8–10]. Most commercially used separators are porous polyolefin membranes, such as the polyethylene (PE) membrane and the polypropylene (PP) membrane, which possess high mechanical strength, excellent chemical stability and appropriate thickness. However, polyolefin membranes often suffer from several shortcomings, such as inferior electrolyte wettability, unsatisfactory porosity, low electrolyte uptake and severe shrinkage at elevated temperatures [3–5,11–15]. The inferior electrolyte wettability, unsatisfactory porosity and low electrolyte uptake will result in the

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Scheme 1. Chloromethylation of PEEK.

elevated internal resistance of the LIB, restricting the electrochemical performance [15,16]. The high shrinkage at elevated temperature usually causes the dangerous thermal runaway of LIB, reducing the operational safety [14,17,18]. Therefore, it is important to exploit an alternative membrane for use as the LIB separator.

The electrospinning method is a promising approach for the preparation of porous membranes [14,16,19,20]. The nonwoven membranes obtained by electrospinning show high porosity, controllable pore size and three-dimensional interconnected microporous structure, endowing the membrane with high electrolyte uptake, shorter ionic pathway and low ionic resistance. Many nonwoven separators with excellent performance have been reported [12,16,19–21], demonstrating the strong potential of the electrospinning method for the fabrication of next-generation separators. Poly(ether ether ketone) (PEEK) has been demonstrated to be an excellent alternative material for the LIB separator [22,23]. The PEEK polymer possesses high thermal and mechanical stabilities benefiting from its robust semi-crystalline aromatic backbones. The polar ether groups and ketone groups exhibit strong interaction with the carbonic ester electrolyte, leading to improved wettability. In addition, the limiting oxygen index (LOI) of PEEK polymer is as high as 36.0–38.0%, implying excellent self-extinguishment in air [24,25] (In contrast, the LOI values of PE and PP are only 17.4% and 18.0%, respectively) (More information is available in Supplementary materials). It is reasonable to conjecture that a PEEK nonwoven membrane should meet the requirements of the next-generation separator.

However, the efforts to process PEEK using electrospinning are hampered by the extreme stability of PEEK, which is a double-edged sword. The melting temperature of PEEK is as high as ~ 334 °C, and PEEK does not dissolve in almost all solvents; both of these findings contradict the requirement for liquid feedstock of the electrospinning method. Even though Andrew et al. [26] have proposed the mixture of concentrated H_2SO_4 and methylsulfonic acid as a solvent to dissolve PEEK, this mixture is too corrosive and dangerous for electrospinning. In our previous research, we demonstrated an indirect method for the processing of the PEEK polymer [23]. PEEK was first modified with chloromethyl groups to achieve good solubility and was later fabricated into a membrane. Finally, the chloromethyl groups were degraded to recover the stability of polymer. This method opens the door to electrospinning the PEEK.

In this study, we fabricate a PEEK-based membrane using the electrospinning method and employ the electrospun nonwoven membrane as the LIB separator. The PEEK-based nonwoven membrane exhibits excellent properties, such as high wettability manifested by the contact angle of 0° , no shrinkage until 180 °C, excellent dimensional stability in various types of solvents (including carbonic ester, chlorohydrocarbon, amides, and concentrated sulfuric acid.) and incombustibility. The LIB using the PEEK nonwoven membrane exhibits good rate performance and satisfactory cycling performance.

2. Experiment

2.1. Materials

PEEK (450 PF, powder) was purchased from Victrex[®] England. Methylsulfonic acid (AR, 99.9%), paraformaldehyde (PFA, AR, 99.9%), anhydrous SnCl_4 (AR, 99.9%), trimethylchlorosilane (TMCISi, AR, 99.9%), deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$), dimethylformamide

(DMF, AR, 99.9%), 1,2-dichloromethane (DCE, AR, 99.9%) and ethanol (EtOH, AR, 99.9%) were purchased from Shanghai Macklin Reagent Co., Ltd. Concentrated sulfuric acid (H_2SO_4 , AR, aqueous solution, 98.2%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Celgard 2400 PP membrane was used for comparison in this study and, for brevity, is referred to as the Celgard membrane.

2.2. Chloromethylation of PEEK

Powdery PEEK (10 g) was dissolved in methylsulfonic acid (600 mL) under vigorous stirring at -10 °C. Next, PFA (13.3 g), TMCISi (30.0 mL), anhydrous SnCl_4 (2.0 mL) and concentrated sulfuric acid (2.0 mL) were slowly added [27]. The mixture was kept at 45 °C for 36 h. Finally, the mixture was poured into 2 L EtOH to precipitate white powder, which was successively washed by abundant EtOH to remove the residual reactants. The obtained white powder was chloromethylated PEEK (CmPEEK) (see Scheme 1). This method eliminates of the use of poisonous chloromethyl ether [28] and the complex multistep reaction [29]. Meanwhile, the methylsulfonic acid can be reused by simply evaporating the EtOH and water from the waste liquor, avoiding the emission of waste acid.

2.3. Fabrication of the nonwoven membrane

Prior to electrospinning, CmPEEK was dissolved in the mixture of DMF and DCE (2:5, volume ratio) to form a 20 wt% solution. The nonwoven membrane was fabricated using an electrospinning machine (Elite-3556H) produced by Beijing Ucalery Co., Ltd. The CmPEEK solution was loaded in a syringe (5 mL) equipped with a $\Phi 0.5$ mm spinneret. A steel roller covered by aluminum foil was employed as the fiber collector. The distance between the spinneret and collector was 20.0 cm. The voltages applied on the spinneret and the collector were $+20.0$ kV and -8.0 kV, respectively. Three syringes were used in parallel to accelerate the electrospinning process, and the injection rate was 0.0667 mL min^{-1} for each syringe. The thickness of the membrane can be controlled by the spinning time, which is 35 μm in this study (30 min). The obtained membrane was compacted by a rolling mill with the pressure of 30 MPa, later dried in air at 140 °C for 24 h, and designated the NW-CmPEEK membrane.

2.4. Conversion of chloromethyl group of the nonwoven membrane

NW-CmPEEK membrane is not suitable for use as an LIB separator because the improved solubility of CmPEEK will cause the collapse of the membrane in the electrolyte. To improve the stability of the nonwoven membrane, the chloromethyl groups should be converted to ether groups using the modified Williamson ether synthesis method [30]. NW-CmPEEK membrane was immersed in a saturated NaOH ethanol solution at 60 °C for 144 h. Next, the membrane was taken out and washed by abundant water to remove the residual NaOH. The chloromethyl group of the CmPEEK polymer was first hydrolyzed to the hydroxymethyl group (OHPEEK). After that step, the hydroxymethyl groups will react with each other to crosslink the polymer (crosslinked PEEK, CPEEK), or be etherified by ethanol (EPEEK) (see Scheme 2). The obtained membrane contained the structures of CPEEK and EPEEK; thus, it was designated the NW-CEPEEK membrane.

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