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Nanofiber-based Matrimid organogel membranes for battery separator

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ABSTRACT

Porous organogel membranes (POMs) composed of electrospun nanofibers with a crosslinking modification have demonstrated great potential as battery separators. As a proof of concept, we fabricated such membranes using electrospun Matrimid nanofibers crosslinked through a room temperature solvent immersion technique. The effects of the crosslinking modification on the chemical structure and mechanical properties of electrospun Matrimid mats were evaluated using Fourier transform infrared spectroscopy and dynamic mechanical analysis tests. Stability was tested on the resulting POMs showing that the crosslinking modification on Matrimid drastically improved fiber chemical and sovothermal resistance.

A Matrimid organogel membrane with a 3-day crosslinking modification was tested as separator in a Li-ion battery. When soaked in dimethylformamide (DMF), no thermal shrinkage was observed at temperature up to 180 °C. At 190 °C and 200 °C, Matrimid membranes showed shrinkage of 10% and 20% with respect to their original sample area, respectively. The discharge capacity of the battery was over 93% after 20 cycles with an average Coulombic efficiency above 98%. The membrane retained physical stability and flexibility after being in contact with the electrolyte $LiPF_6$ in EC-DEC-DMC for three weeks of testing and demonstrated great potential as battery separators in applications involving strong solvents and high temperature.

1. Introduction

Electrospinning is an old technology that had remained dormant as an area of research until recently, with great interest generated by the surge in applications of nanotechnology [1]. Fibers produced from electrospinning are tunable from nanometers in diameter to several micrometers [2]. This highly tunable fiber diameter along with tunable morphologies and the ability to use virtually any soluble polymer to produce fibers has been stimulating research interest in many fields including liquid separations, sensors, tissue scaffolding, and air filters [3]. Another promising field for nanofiber-based materials are as separators for lithium-ion batteries [4,5]. Nevertheless, an unfortunate drawback preventing this technology from further applications is the necessity of using soluble polymers, leading to an inherent inability to use unmodified nanofibers for applications requiring strong solvents. Nanofiber mats possess properties that would allow these materials to excel in applications involving strong solvents such as organic solvent filtrations, battery separators, and membrane distillation with higher chemical resistances. A handful of studies have shown the cross-linking of polymers to increase chemical resistance and application durability such as poly(vinyl cinnamate) for growth of zirconium-based metal-organic frameworks [6], poly(ethylene oxide) for oil/water separation [7], and poly(Vinyl alcohol) for microscaled-particles filters [8]. However, these works either only introduce water resistance, or are composed of polymers that are not as commercially desirable as other materials.

Porous organogel membranes (POMs) with high surface area by incorporating a crosslinking step to electrospun mats should increase the tunability and functionality of the electrospun polymer mats just as crosslinking does to traditional polymeric gels. In this work, Matrimid 5218 (hereafter simply referred to as Matrimid), a highly-produced, commercial available polymer, was selected for electrospinning, which is a crosslinkable polymer from the polyimide family that has been electrospun for a variety of applications including fuel cell membranes [9], membrane distillation [10], and as carbon nanofiber precursors [11]. The incredibly versatile Matrimid resin in a traditionally casted film form is studied and used commercially for many applications including gas separation [12–14] and solvent filtration membranes [15]. However, although Matrimid has been crosslinked in a film form [16,17], notably for organic solvent nanofiltration applications [18], and has been electrospun [10,11,19,20], the two techniques have not been combined, and resulting properties have not been determined.

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Proven versatility and commercial-scale production of Matrimid makes it a natural and potentially archetypal polymer for electrospinning and crosslinking as the technology evolves and matures. For this reason, this work focuses on the crosslinking of electropun Matrimid mats with para-xylylenediamine to produce a series of POMs. Organogels are fluid-filled structures as predominantly contain an organic continuous phase. By forming a three-dimensional crosslinking network, polymers have the ability to retain organic solvents and create semi-solid systems [21–23]. Key properties concerning application and design of Matrimid gels are analyzed for multiple crosslinking densities including stability tests and gel swelling. Matrimid nanofiber mats are then used as a battery separator. The separator is one of the most critical parts of lithium ion batteries, which separates the positive and negative electrodes to prevent electrical short circuits while permitting free flow of lithium ions and isolating electronic flow [24–27]. Commercially, polyethylene (PE), polypropylene (PP), or their blends, are used as separators in lithium ion batteries [24,28]. The poor thermal stability of these polyolefin porous membranes leads to thermal shrinkage when used under elevated temperatures: generating safety concerns [29,30]. On the other hand, safety and cycle life of the battery are affected by the required use of very thin and highly porous separators because their mechanical strength is reduced.

In order to satisfy these needs, battery separators can be designed and obtained from non-woven membranes as they have more alternatives in compositions and structure than polyolefin (PE, PP) membranes [29]. Non-woven separators obtained by electrospinning are characterized by high porosity and large pore size [27]. Moreover, studies made in electrospun polyimide nanofibers show an exciting superior thermal stability and mechanical and electrochemical performance when used as separators for lithium ion batteries [4,31].

The polyimide Matrimid has a glass transition temperature of 338 °C [32], and a degradation temperature of 465 °C [33], which can effectively avoid the short circuits caused by the shrinkage of the conventional separators at high temperature of 150 °C [4]. Based on these chemical properties, Matrimid nanofibers are placed in an electrolyte solution composed of the strong solvent $LiPF_6$ in EC-DEC-DMC, and 20 charge/discharge cycles are ran to further confirm the synthesized Matrimid POM are capable of continued performance in strong-solvent systems.

2. Materials and methods

2.1. Preparation of Matrimid nanofiber organogel

Solutions of 12 w/w% Matrimid/DMF were prepared and fed through a metallic needle by a syringe pump (New Era Pump Systems, Inc. NY, USA) at the rate of 0.6 mL h^{-1}. A 5-cm circular 100 mesh 304 stainless steel filter was used as a collector. A voltage of 22 kV (Gamma High Voltage Research) was applied between the spinneret and the collector with a distance of 23 cm at room temperature. To obtain test samples with structures matched as much as possible, all electrospun nanofibrous mats were produced from 0.12 mL of the electrospinning solution, except for the membranes used for the battery test which were produced from 1.2 mL of the Matrimid/DMF solution in order to increase the thickness. The spun-nanofibers mats were collected and stored at room temperature until use.

Crosslinking modification was performed as reported by Tin et al. [16]. Crosslinking reagent solutions of 10% (w/v) para-xylenediamine/methanol were prepared. Electrospun Matrimid membranes were immediately washed with fresh methanol after 0.5, 3, 12, 24, and 72 h to quench the crosslinking reaction and remove residual reagents. Samples were dried at room temperature overnight before tests.

2.2. Characterization

The IR spectra of membranes were obtained at room temperature by a Nicolet iS50 FT-IR with a DTGS detector (Thermo Scientific, USA). Each image is an average of 100 scans in the range 1900–600 cm^{-1}, a background was taken immediately preceding each measurement.

SEM images were taken on a Zeiss EVO MA 10 at 18.00 kV. The non-metallic samples were sputtered with gold and placed on copper tape for analysis.

Optical Profilometry was carried out with a 20x lense on a ZeScope Optical Profilometer machine. The tape substrate was considered level and the data was normalized to its slope. To prepare samples, each was pressed onto flat double sided copper tape intended for SEM, and attached to glass substrate. The fibers were carefully saturated in acetone and dried to set the fibers flat over the copper tape.

2.3. Mechanical and stability tests

The DMA (Dynamic Mechanical Analysis) test used a Discovery HR2 Hybrid Rheometer (TRIOS software - TA Instruments) testing each sample in triplicate with a crosshead speed of 50 μm/s. Sample preparation was carried out using the method described by Tan et al. [34].

The stability of the nanofibers was tested by exposing the Matrimid mats to air and DMF; nanofibers exposed only to air were placed in a Petri dish, while nanofibers and DMF were sealed in a 50 mL Teflon lined autoclave. Samples were kept at room temperature, 100 °C, and 150 °C for 24 h, and then slowly cooled to room temperature. Analysis of the mats was conducted by using digital photographs taken by a MicroCapture Pro microscope (Celestron).

2.4. Battery test

Matrimid membranes that underwent a 3-day crosslinking modification were tested as battery separators. These membranes were placed in a vacuum drying chamber at 75 °C overnight to get rid of crosslinking reagent residual before being used to assemble the cells.

The separators were sufficiently soaked in a liquid electrolyte consisting of 1.0 M $LiPF_6$ in ethylene carbonate (EC)-diethyl carbonate (DEC)-dimethyl carbonate (DMC) (4/2/4 by weight) in an argon-filled glove box. The electrolyte soaked separators were sandwiched between a natural graphite anode and a $LiCoO_2$ cathode of 4 cm^2 in area and assembled into blocking-type cells. A BT2000 Battery Test Equipment (Arbin Instruments, TX, USA) was used to evaluate the C-rate capability and cycling performance of the cells. For the measurement of cycling performance, the cells were cycled at a constant charge/discharge current density of 0.1 C/0.1 C for 20 cycles under a voltage range between 2.5 and 4.2 V.

The thermal shrinkage of the Matrimid separators was determined by measuring the change in area of 1 cm^2 – separator that underwent heat treatment at 120, 150, 170, 180, 190, and 200 °C for 0.5 h. The shrinkage percent was calculated using the following equation (S_0 and S stand for the area of separator before and after heat treated, respectively):

$$Shrinkage\ \% = \frac{S_0 - S}{S_0} \times 100 \quad (1)$$

3. Results and discussion

3.1. Matrimid crosslinking and Mechanical strength

Electrospun Matrimid mats were crosslinked for 0, 0.5, 3, 12, 24 and 72 h through room temperature solution immersion. Fig. 1**a** shows a two part reaction scheme for the crosslinking of Matrimid; amino groups in para- xylylenediamine attack the imide functional groups of Matrimid. FTIR peaks after varying crosslinking times are shown in Fig. 1**b**.

The pure Matrimid film exhibited peaks at 1780, 1728, 1674, 1511, 1488, 1375, 1096, 721 cm^{-1}. Asymmetric and symmetric C=O