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The high performances of SiO_2/Al_2O_3-coated electrospun polyimide fibrous separator for lithium-ion battery

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ABSTRACT

A SiO_2/Al_2O_3-coated electrospun PI membrane was prepared by means of simple dip coating of Al_2O_3 and SiO_2 mixture onto electrospun PI membrane. The electrochemical performance of the membrane was tested as a separator in the lithium-ion batteries and compared with those of PI membrane, Al_2O_3-coated PI membrane, SiO_2-coated PI membrane, trilayer SiO_2/Al_2O_3-coated PI membraneand Celgard 2400 separators. The SiO_2/Al_2O_3-coated electrospun PI membrane exhibits the best electrochemical performance, including the cycling performance and rate capability. The optical mass ratio of SiO_2/Al_2O_3 was 2:1. The SiO_2 component on the interface decrease the interface resistance. Meanwhile, Al_2O_3 component increase the ionic conductivity. Owing to the intrinsic thermal stability of ceramic materials and PI, the composite membrane doesn't have the thermal shrinkage problem of commercial separators.

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1. Introduction

With the growing popularization of electric vehicles and portable electronics, lithium-ion batteries (LIBs) are expected to achieve high energy density at high power density [1–3]. The LIB performances are strongly depended on the performances of electrode materials and separators. Recently, the most commonly used separator materials are polyolefin, such as polyethylene (PE), polypropylene (PP) and their compounds [4]. However, polyolefin separators are limited used as high power battery separator due to the poor electrolyte wettability and relatively low thermal stability [5,6].

Electrospinning is reported as one of the efficient method to improve the wettability performance as the crystallinity of the fibers are low since the drying process of the fibers occurs in less than 0.1 s. So far, only a few polymer were reported as electrospun separator candidates, including polyacrylonitrile (PAN) [7], Polyvinylidenefluoride (PVDF) [8], polyethylene terephthalate (PET) [9], polyimide (PI) [10] and polyvinyl chloride (PVC) [11]. High porosity and larger nonwoven pores can offer excellent wettability and electrochemical properties. However, most of the electrospun separator has to be thicker since larger porous structure causes short circuits easily if the membrane is too thin. It has limited capability in stabilizing the battery capacity during high discharge rate due to polymer degradation and the leakage of organic liquid electrolyte which only exhibit macroporous structures (pore size $> 1\ \mu m$) and do not have mesoporous structures ($2\ nm < pore < 50\ nm$) [12]. In addition, the mechanical strength of the electrospun fibrous membrane is pore as the low crystallinity and weak bonding between fibers [13].

To improve the stability of the LIB, inorganic nanoparticles are considered. As reported, addition of inorganic nanoparticle could adsorb hydrogen fluoride in electrolyte during charge/discharge cycles [14,15]. Due to the porous surface and capillary effect of inorganic oxide particles composite membrane the composite membrane has excellent wettability and can absorb a lot of liquid electrolyte, which has good ionic conductivity. Rao et al. prepared polyethylene-supported poly(acrylontrle-*co*-methylmethacrylate)/nano-Al_2O_3 microporous composite polymer electrolyte for lithium ion battery, Ionic conductivity was improved to $3.2{*}10^{-3}\ S\ cm^{-1}$, decomposition potentials enhanced 5.7 V (vs Li/Li^+), and interface impedance on lithium is reduced $160\ \Omega\ cm^2$ [16]. Wang et al. prepared an uniform nano composite separators by dispersing and ball milling of Al_2O_3 powders in the poly(vinylidene fluoride) polymer, exhibiting high thermal stability and excellent electrochemical performance [17]. Jeong et al. investigated performance SiO_2/PVDF-HFP composite separators [18].

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In this paper, a nano Al_2O_3/SiO_2 particles coated electrospun PI fibrous membrane was developed as a high performance LIB separator. The high thermal stability electrospun PI nanofibrous membrane was used as a scaffold. The coated nano Al_2O_3/SiO_2 particles seal the pores on the top layer of the membrane. The larger pores from the nonwoven structure work as an electrolyte storage tank. Such a structure is essential to enhance the wettability of the separator and stability of the electrolyte in the separator. As the top layer of the membrane was sealed with nanoparticles, the thickness of the membrane can be thinner than the pure electrospun separator without any safety issue for high-power LIBs. The composite separator characteristics were based on the morphology, thermal stability, pore-size distribution, infrared analysis, the charge/discharge property, and cycle performance. Celgard 2400 separator was used for comparison.

2. Experimental

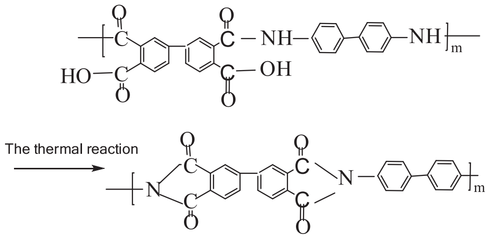
2.1. Materials

3,3′,4,4′-Biphenyl tetracarboxylic diandhydride (BPDA, > 99.5%, Changzhou SunChem Chemical Co., Ltd), *p*-phenylenediamine (PPD, > 99%, Wuxi ChanganFine Chemical Factory), *N*,*N*-dimethylformamide (DMF, > 99.5%, West Long Chemical Co., Ltd), SiO_2 (30 ± 5 nm, Hangzhou Wanjing New Material Co., Ltd), Al_2O_3 (20 ± 5 nm, Hangzhou Wanjing New Material Co., Ltd), 1-methyl-2-pyrrolidinone (NMP, > 99.99%, Shenzhen Kejing. Ltd), Polyvinylidene Fluoride (PVDF, ≥ 99.5%, Shenzhen Kejing. Ltd). All materials are commercially available and used without further purification. The Celgard membrane (Celgard 2400, Shanxi Power Battery Material Co., Ltd) with thickness of about 20 μm was used as the membrane of LIBs for comparative study.

2.2. Preparation of the modified composite membrane

All of the polyamic acid (PAA) spinning solutions were prepared in DMF and polymerization step was done according to the literature [10,19]. Electrospinning was carried out at the supply rate of 0.8 mL h^{-1}, 15–25 kV on the spinneret, and 30 cm distance between the spinneret and the collector. The electrospun PAA fibrous membrane with 30 μm thicknesses were collected within 2 h. As-spun fibers were imidized in a horizontal tubular furnace.

The thermal reaction of polyimide fiber from polyamide acid fiber was shown as follows:



The imidization was carried out by the following program: heating up to 250 °C for 30 min and held for 30 min; heating up at rate of 1 °C per min to 370 °C and held for 30 min; turning off the furnace and cooling down to room temperature.

Nano SiO_2, Al_2O_3 and SiO_2/Al_2O_3 mixture was dip-coated on the surface of the prepared PI membrane. The dip-coating solution was prepared with 0.8 wt% nanoparticle dispersed in a 0.8 wt% PVDF/NMP solution. The mass ratio of Al_2O_3 and SiO_2 was set as 2:1, 1:1 and 1:2 in the mixture.

The PI membrane was immersed into solution for 2 min, hanging and airing. The mass ratio of PI and SiO_2 was about 1:1 by comparing mass before and after immersing in our experiment. The sample coated Al_2O_3 in the inner layer and SiO_2 in the outer layer is labeled as SiO_2–Al_2O_3-coated PI membrane; The sample coated SiO_2 in the inner layer and Al_2O_3 in the outer layer is labeled as Al_2O_3–SiO_2-coated PI membrane. All the membranes were drying under vacuum of 120 °C for 5 h before using.

2.3. Structure characterization

The surface morphology and fiber diameters of the samples were investigated using a scanning electron microscope (SEM, LEO1530). The porosity and pore size distribution of membranes were determined by mercury porosimeter (AutoPore IV 9500). The thermostability of the samples was measured with differential scanning calorimetry (DSC, Q2000) at a heating rate of 10 °C min^{-1} under N_2 flow. Thermogravimetry (TGA Q5000) was performed under N_2 flow at a heating rate of 10 °C min^{-1}. Crystallinity was examined with X-ray diffractometer (XRD, D/MAX-RM2000, Rigaku) at a rate 5 ° min^{-1}.

2.4. Electrolyte uptake measurements

Liquid electrolyte uptakes of the SiO_2/Al_2O_3-coated PI membrane was measured in 1 mol L^{-1} $LiPF_6$ (EC:DMC:EMC=1:1:1) solution at room temperature inside the glove box for 6 h. Liquid electrolyte–soaked membranes were weighed immediately after removing the excrescent surface electrolyte by wipes. The liquid electrolyte uptakes were calculated as follows:

$$\text{Electrolyteuptakes}(\%) = (M_1 - M_0)/M_0 \times 100\%$$

where M_0 and M_1 were the weight of the membrane before and after immersion in the liquid electrolyte, respectively [20].

2.5. Electrochemical performance evaluation

All Electrochemical characterization of the SiO_2/Al_2O_3-coated PI membrane was measured in a coin-type cell (CR 2032). The ionic conductivities, electrochemical window and the interfacial resistance evaluation of different separators were measured using an electrochemical workstation (CHI 600).

SiO_2/Al_2O_3-coated PI membrane was sandwiched between two stainless steel plates and sealed in a cell can for ionic conductivity measurement. The AC impedance spectra was measured over an AC oscillation of 10 mV frequency range of 1 Hz to 100 kHz in the room temperature. The ionic conductivity was calculated using the following equation:

$$\sigma = d/R_b S$$

Here, σ is the ionic conductivity, R_b is the bulk resistance, and d and S are the thickness and area of the specimen, respectively [21].

Linear sweep voltammetry tests were conducted. The membrane was sandwiched between a stainless steel working electrode and lithium metal counter electrode at a scan rate of 10 mV s^{-1} from 2.5 V to 6.0 V versus Li/Li^+ to check oxidative decomposition [21]. The interfacial resistance between lithium electrode was determined from the ac impedance spectrum recorded for Li ∣ separators ∣ Li cell. The measurement was carried out over a frequency range of 65,000 Hz to 0.01 Hz, with an amplitude of 10 mV.

A coin-type cell (CR 2032) was used in half-cell configuration assembled in a configuration of $LiFePO_4$∣ separator ∣ Li to investigate the rate capability for the cell with various membranes. During the rate-performance tests, the cell was cycled at a charge/discharge current density of 0.2, 0.5, 1, 2, 5, 10, 15, 20 C under a voltage range between 2.0 and 4.0 V. The cycle performance was investigated at rate of 5 C for 250 cycles. The cells of Al_2O_3–SiO_2-coated PI membrane, SiO_2–Al_2O_3-coated PI membrane

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