



# A nano-silica modified polyimide nanofiber separator with enhanced thermal and wetting properties for high safety lithium-ion batteries



Ying Wang, Suqing Wang\*, Junqi Fang, Liang-Xin Ding, Haihui Wang\*

School of Chemistry & Chemical Engineering, South China University of Technology, Guangzhou 510640, China

## ARTICLE INFO

### Keywords:

Lithium-ion batteries  
Electrolyte wettability  
Safety  
Separator  
LiMn<sub>2</sub>O<sub>4</sub>

## ABSTRACT

The commercial polyolefin separators still possess two well-known drawbacks: poor wettability and thermal stability. Herein, a thin and lightweight silica filled in polyimide (PI) nanofibers membrane is prepared by electrospinning. Without any binders, the nano-silica particles are firmly embedded in the PI nanofibers with high structure stability. The PI-SiO<sub>2</sub> membrane with high porosity (90%) presents enhanced conductivity due to the excellent electrolyte wettability and large electrolyte uptake (about 2400%). In addition, the PI-SiO<sub>2</sub> membrane displays good mechanical flexibility and enhanced thermal stability up to 250 °C, which significantly improve the safety of lithium-ion batteries when used as a separator. The LiMn<sub>2</sub>O<sub>4</sub>/Li cell with the PI-SiO<sub>2</sub> separator exhibits highly improved rate capability and cycling stability at different temperatures (25 °C and 55 °C), which make PI-SiO<sub>2</sub> membrane as a promising secure separator candidate for high-performance and safety lithium-ion batteries.

## 1. Introduction

Due to high energy density, long cycle life, and environmental friendliness [1–3], lithium-ion batteries (LIBs) not only successfully applied to cell phones, laptops and digital cameras but also garnered the most promising candidates for electric vehicles and energy storage systems (ESSs) [4–6]. In order to satisfy expanded applications of batteries, reliable electrochemical property and reinforced safety tolerance are essentially required. Separator plays the vital role of safety by preventing physical contact of the cathode and anode electrodes as well as influencing the transfer of lithium ions inside the cell [7]. Current commercial separators for LIBs are porous polyolefin membranes, which made from polyethylene (PE) or/and polypropylene (PP). Those separators are reliable for most portable electronic applications due to their good chemical stability with electrolyte and mechanical strength [8,9]. However, polyolefin separators have two intrinsic limitations. One is the low porosity which induces the poor wettability with organic electrolyte and generates high ionic conduction resistance in the interfacial layer of separator and electrodes [9,10]. The other is the unsatisfactory thermal stability due to the low melting point of polyolefin, which leads to an internal short circuit between electrodes and even causes a fire or explosion at elevated temperatures [11].

Recently, numerous approaches have been adopted to overcome the aforementioned problems. For example, previous studies have demon-

strated that grafting polymers (poly(ethylene oxide) and poly(methyl-methacrylate)) on the polyolefin separators could generate a stable coating layer and effectively enhanced the wettability due to the high polarity and affinity between electrolyte and polymer [12,13]. However, this method reduces porosity of the separator and induces poor electrolyte uptake. The emergence of non-woven membranes fabricated by electrospinning can highly increase the porosity of the separator and enhance the electrolyte uptake [14–16], but the poor thermal stability still limits their applications at high temperature. Generally, inorganic ceramic particles which possess the merits of thermal stability and hydrophilicity have been introduced into polymer separators [17]. For instance, Kim et al. developed a ceramic-coated polyethylene (PE) separator using dip-coating method, which achieved good thermal stability (160 °C) and wettability for liquid electrolyte [18]. Yang et al. synthesized a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-coated electrospun polyimide fibrous separator with high porosity and electrolyte uptake, exhibited good electrochemical performance [19]. Unfortunately, the introduction of inorganic coating layer inevitably increased the thickness and weight of the separator [17]. More seriously, the binders used to form the ceramic coating layer showed a high shrinkage at elevated temperature, resulting in particles shedding from separators and influencing the film-forming properties [20].

Herein, we developed a novel flexible thin PI-SiO<sub>2</sub> composite membrane integrating with the comprehensive merits of high electrolyte affinity, excellent dimensional and thermal stability. Because of the

\* Corresponding authors.

E-mail addresses: [cesqwang@scut.edu.cn](mailto:cesqwang@scut.edu.cn) (S. Wang), [hhwang@scut.edu.cn](mailto:hhwang@scut.edu.cn) (H. Wang).

slight amounts of SiO<sub>2</sub> nanoparticles tightly embedded in the polyimide nanofibers, the membrane shows a negligible thickness and weight increase, and simultaneously maintains an outstanding structural stability. Notably, the PI-SiO<sub>2</sub> membrane with high polarity and porosity shows significantly enhanced electrolyte wettability, and then effectively facilitates the transport of lithium ions. More importantly, due to the excellent mechanical and heat tolerance of SiO<sub>2</sub> and PI [21–23], the PI-SiO<sub>2</sub> hybrid membrane displays excellent dimensional flexibility and good thermal stability. The LiMn<sub>2</sub>O<sub>4</sub>/Li cell using PI-SiO<sub>2</sub> separator exhibits excellent electrochemical properties with better rate capability (80 mA h g<sup>-1</sup> at 5 C) and more stable cycling performance, surpassing that of using commercial PP separator.

## 2. Experimental section

### 2.1. Preparation of membranes

SiO<sub>2</sub> with particle size of 15 nm was purchased from Alfa Aesar, 4,4'-oxydianiline (ODA), pyromellitic dianhydride (PMDA), and dimethylformamide (DMF) were supplied by Sinopharm Chemical Reagent Co., Ltd, China. ODA (7.924 g, 0.039 mol) was first dissolved in 95 ml DMF. After ODA completely dissolved, PMDA (8.805 g, 0.04 mol) was divided into four equal parts and added into the system step by step with intense mechanical stirring at 0 °C for 3 h. Then SiO<sub>2</sub> nanoparticles (0.836 g) was dispersed in DMF (5 ml) and added into the system to obtain pristine polyamic acid (PAA) solution containing 5 wt % SiO<sub>2</sub>. Electrospinning process was conducted at 15 kV using a syringe with a stainless steel needle with a diameter of 0.23 mm, the working distance was set as 15 cm. The as-spun PAA-SiO<sub>2</sub> membrane was imidized at high temperature to obtain the PI-SiO<sub>2</sub> membrane using the following program: heating up to 100, 200, and 300 °C at a rate of 2 °C min<sup>-1</sup> and isotherming at each temperature for 2 h in vacuum. For comparison, the PI membrane was fabricated without adding of SiO<sub>2</sub> nanoparticles.

### 2.2. Material characterizations

The surface and cross-sectional morphologies were characterized using scanning electron microscope (SEM, Hitachi SU8000) and transmission electron microscopy (TEM, JEOL 2100F). Elemental analysis was performed on an Elementar Vario EL cube. Thermogravimetric (TG) analysis was scanned from 25 to 1000 °C at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere using a NETZSCH STA44C. Differential scanning calorimetry (DSC) measurement was carried out from 30 to 500 °C at a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere (NETZSCH DSC 214). The air permeability of separator was characterized by a Gurley-type densometer (4110N, Gurley). Mechanical properties of membranes (membrane size: 20 mm × 40 mm) were tested using Instron-5565 at a stretching speed of 1 mm min<sup>-1</sup>. The wetting property of the separator was tested using a contact angle tester (Dataphysics OCA40 Micro). Electrolyte immersion-height test was evaluated by measuring the absorbed electrolyte height of separator at room temperature for 1 h. The porosity of the membrane was tested by a liquid absorption and calculated according to the equation:

$$\text{Porosity} = \frac{W_w - W_d}{\rho V} \quad (1)$$

Where  $W_d$  is the weight of dry separator,  $W_w$  is the weight of the separator absorbed hexadecane for 1 h, while  $\rho$  and  $V$  represent the density of the hexadecane and the volume of the separator, respectively [24].

The electrolyte uptake and retention of the separator were calculated by weighting the separator.  $W_0$  is the pristine weight of separator. After soaking in the electrolyte for 1 h, the separator was taken out and weighed ( $W_1$ ) again. Last, the separator was stored at 50 °C and measuring the equilibrium weights ( $W_x$ ) for different periods of time.

The electrolyte retention and electrolyte uptake of the separator were calculated as follows [25]:

$$\text{Electrolyte retention} = \frac{W_x - W_0}{W_1 - W_0} \times 100\% \quad (2)$$

$$\text{Electrolyte uptake} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (3)$$

To measure the ionic conductivity, the separator with electrolyte was tested by sandwiching between two stainless steel (SS) electrodes. The ionic conductivity was calculated as follows:

$$\sigma = \frac{d}{R_b \cdot S} \quad (4)$$

Where  $d$  is the thickness of the separator,  $S$  is the area of SS electrodes, the bulk resistance ( $R_b$ ) of the separator was obtained from electrochemical impedance spectroscopy (EIS) by Zahner IM6ex electrochemical workstation with the frequency range from 100 kHz to 1 Hz [25].

### 2.3. Electrochemical characterizations

In order to check the electrochemical stability of membranes, the linear sweep voltammetry (LSV) was conducted. The membrane was sandwiched between lithium metal counter electrode and stainless steel working electrode at a scan rate of 1 mV s<sup>-1</sup> from the open circuit potential (positive scan and negative scan, respectively). The CR2025 coin cell was assembled in an argon-filled glove box. The cathode was prepared by coating a slurry consisting of 80 wt% LiMn<sub>2</sub>O<sub>4</sub> (Huizhou Desay Battery Technology Co., Ltd.), 10 wt% super P and 10 wt% PVDF in N-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd, China) on the aluminum foil and vacuum dried at 80 °C for 8 h. The electrolyte was 1 M LiPF<sub>6</sub>/ethylene carbonate (EC) + dimethyl carbonate (DEC) (1:1, v/v). The discharge and charge measurements were conducted on a NEWARE battery tester (Shenzhen, China) in a voltage range of 3.5–4.3 V (vs. Li<sup>+</sup>/Li).

## 3. Results and discussion

Fig. 1 shows the morphologies of the PI and PI-SiO<sub>2</sub> membranes. A large area membrane of more than 30 cm × 11 cm can be easily fabricated, which is beneficial to practical applications (Fig. S1). The cross-sectional SEM images (Fig. 1a and d) show that the average thickness of PI and PI-SiO<sub>2</sub> membranes is about 20 μm. The thickness can be easily adjusted by electrospinning time. Both PI and PI-SiO<sub>2</sub> membranes feature interconnected nanofibrous structure and the diameter of the nanofibers is about 250 nm (Fig. 1b and e). The high-magnification SEM image and TEM image of the PI-SiO<sub>2</sub> nanofiber (inset of Fig. 1e and f) demonstrates that the SiO<sub>2</sub> nanoparticles almost homogeneously scatter in the PI nanofibers. Furthermore, elemental mapping results of the PI-SiO<sub>2</sub> membrane (Fig. S2) present a uniform distribution of elements. To verify the lightweight of PI-SiO<sub>2</sub> membrane, the mass densities of the membranes are tested and shown in Table S1. The PI-SiO<sub>2</sub> membrane exhibits much lower mass density than PP membrane.

The porosity of the membrane was tested by liquid absorption method [24]. The porosities of PI (91%) and PI-SiO<sub>2</sub> membranes (90%) are much higher than that of PP membrane (45%), owing to the well-developed pores formed by interconnected nanofibrous structure. The air permeability reflects the mobility and transportation ability of the lithium ions in the membranes, which can be represented by the Gurley value [9]. It should be noted that the Gurley values of PI and PI-SiO<sub>2</sub> membranes (5 s per 100 cm<sup>3</sup>) are much lower than PP membrane (15 s per 100 cm<sup>3</sup>) under pressure of 0.02 MPa, verifying the multi-porous structure of the membranes and a fast transportation of lithium ions in the PI and PI-SiO<sub>2</sub> membranes.

Contact angle measurement with liquid organic electrolyte was

Download English Version:

<https://daneshyari.com/en/article/4988834>

Download Persian Version:

<https://daneshyari.com/article/4988834>

[Daneshyari.com](https://daneshyari.com)