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A highly safe and inflame retarding aramid lithium ion battery separator by a papermaking process ☆

Jianjun Zhang [a], Qingshan Kong [a], Zhihong Liu [a], Shuping Pang [a], Liping Yue [a,b], Jianhua Yao [a], Xuejiang Wang [a], Guanglei Cui [a,*]

[a] Qingdao Key Lab of solar energy utilization and energy storage technology, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China
[b] College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

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ABSTRACT

An aramid membrane with good electrolyte wettability, high ionic conductivity, excellent inflame retarding property and superior thermal resistance has been successfully fabricated via a facile papermaking process for improving the safety characteristic of lithium ion battery. The aramid membrane endows the lithium cobalt oxide ($LiCoO_2$)/graphite cell superior cycle performance and better interfacial flexibility. In addition, the lithium iron phosphate ($LiFePO_4$)/lithium cell using such aramid membrane exhibited stable charge–discharge profiles and satisfactory cycling stability even at an elevated temperature of 120 °C. These fascinating characteristics and facile papermaking method provide potential application as separator in high energy lithium ion battery.

1. Introduction

Due to its high energy and power characteristics, lithium ion battery has attracted extensive attention for high-power tools and portable electronic applications [1–7]. Lithium ion battery separator plays a determinant role in safety issues, which is to allow fast transport of ionic charge and prevent electrical short circuits between cathode and anode. Currently, most commercial separators in lithium ion battery are typically made of polyolefin materials, such as polyethylene (PE), polypropylene (PP) and their blends. These separators possess many advantages such as electrochemical stability, proper mechanical strength and thermal shutdown properties [8–10]. However, their poor thermal shrinkage, low porosity and inferior electrolyte wettability have often aroused some serious concerns about their future application in electric vehicles, as far as safety issues and long-term application of electric vehicles is concerned. Since commercial polyolefin separators might thermally runway in case of malfunction of the battery, highly safe separators must be urgently explored. Remarkable efforts have been invested to solve the aforementioned challenges, which include the coating of nanoparticles to enhance interfacial stability [11–15] and exploring the nanofiber nonwovens [16–23]. Unfortunately, the problem of unbounded inorganic nanoparticles still exists and the latter normally suffers from poor mechanical strength. In addition, polyolefin as scaffold still suffer from thermally runaway risks owing to a poor thermal resistance. So it is obligatory for us to find out a promising technique for the fabrication of robust and highly safe separator.

Most of the commercially available polyolefin separators are made of PE, PP or their mixtures through either dry or wet process [10,24]. Both processes include an extrusion step to make thin films and employ one or more orientation steps to impart porosity and increase the tensile strength. Separators made by the dry process generally undergo thermal shrinkage along the machine direction at elevated temperature, while those prepared by the wet process exhibit relative high cost. The most widely used processes for manufacturing nonwoven separator are electrospinning method and melt-blown technology. [25–27]. Non-woven separators produced by electrospining method are featured by a high porosity and uniform pore size. However, this kind of membrane shows low mechanical strength. Separators made by melt-blown technology exhibits good mechanical properties, but it suffered from excessively large-sized pores, which was not beneficial to maintain the battery voltage due to self-discharge and also vulnerable to breakdown at high discharge rates or under vigorous conditions. Microporous polymer membrane was also obtained by phase inversion process [28,29], which requires a lot of organic solvent and then generates extra cost. It is well known that papermaking technique has been demonstrated to be an efficient procedure to fabricate nonwoven membrane. The preparation of bamboo fiber and PP composite membrane was carried out

* Corresponding author. Tel.: +86 532 80662746; fax: +86 532 80662744.
E-mail address: cuigl@qibebt.ac.cn (G. Cui).

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via papermaking method to solve the dispersion problem of bamboo fiber [30]. It was also proved that papermaking technology is an effective way to achieve large-scale production of composite membrane [31,32]. Aramid possessing excellent mechanical properties, inflame retarding, superior heat resistance and electric insulating property are widely used as high temperature filter material, electrical insulation and high-temperature protective clothing [33–36]. It is expected that aramid lithium ion separator could deliver a superior thermal resistance, inflame retarding and high safety characteristic especially for electrical vehicle applications [37]. So far, there is rare report on exploring aramid membrane as lithium ion battery separator via a papermaking process. Herein, a major objective of this work is to explore aramid membrane as highly safe lithium ion battery separator. It is demonstrated that such membrane exhibits desirable heat resistance, excellent electrochemical stability and good battery performance, which render aramid membrane the feasibility to serve as a promising separator for high energy lithium ion battery.

2. Experimental

2.1. Materials

Aramid short fibers and aramid pulps were purchased from DuPont Company. PP separator (Celgard 2500) was purchased from Celgard Company. Other chemical reagents were all purchased commercially and used without further purification.

2.2. Preparation of the aramid membrane

A schematic illustration for preparation of the aramid membrane was shown in Fig. 1. The aramid short fibers (146 g) and aramid pulps (219 g) were soaked with 20 L water and pulped for 2 h to form completely dispersed fiber suspension, then the wet aramid sheet was made on a papermaking machine. The formed wet sheet was transferred to a plate dryer to remove additional water. Hot calendering was further carried out, which temperature and pressure was set to 240 °C and 14 MPa, respectively. The final aramid membrane was dried under vacuum at 50 °C for 24 h.

We can fabricate aramid membrane with different thickness by adjusting the grammatura (g/m^2). For example, we obtained aramid membrane with 75 μm when the grammatura was 35 g/m^2. Correspondingly, we can prepare membrane with different thickness by adjusting the grammatura.

2.3. Membrane characterization

The surface morphology of separators was observed by a Hitachi S-4800 field emission scanning electron microscope (SEM) [38]. The porosity of the separators can be measured using n-butanol absorption method [39]. For this purpose, the mass of the separators was measured before and after immersion in n-butanol for 2 h. The porosity of the membrane was calculated using the equation: porosity $= (m_b / \rho_b) / (m_b / \rho_b + m_p / \rho_p) \times 100\%$, where m_b and m_p are the mass of n-butanol and the separator and ρ_b and ρ_p are the density of n-butanol and the separator, respectively. For example, we used density of PP material to calculate the porosity of PP separator. Meanwhile, we used density of aramid material to calculate the porosity of aramid membrane. The air permeability of the separators was examined with a Gurley densometer (4110 N, Gurley) by measuring the time for air to pass through a determined volume (100 cc) [40]. The electrolyte uptake was obtained by measuring the weight of separators before and after liquid electrolyte soaking for 2 h and then calculated using following equation: electrolyte uptake $= (W_f - W_i) / W_i \times 100\%$, where W_i and W_f are the weights of the separator before and after soaking in the liquid electrolyte, respectively [41].

The mechanical property was measured using an Inston-3300 universal testing machine (USA) at a stretching speed of 1.66 mm s^{-1} with the sample straps of about 1 cm wide and 8 cm long [42]. To evaluate its thermal shrinkage behavior, the separators were placed in an oven and heated at 250 °C for 0.5 h [43]. Thermal resistance of the separators was examined by a differential scanning calorimeter (Diamond DSC, PerkinElmer) in a temperature range from 50 °C to 300 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere [44]. Limiting oxygen index (LOI) measurements were undertaken using a JF-3 type instrument (China). Specimens of dimensions 100 mm × 100 mm × 10 mm were used for the LOI tests [45]. The specimens of LOI tests were prepared as follows: First, we tailored aramid membrane to form a certain size (1600 mm × 800 mm × 0.075 mm) of the membrane; and second, we fold obtained membrane four times in the length direction and then fold three times in the width direction to get aramid specimen of dimensions 100 mm × 100 mm × 10 mm. The preparation process of PP specimen was using the similar method.

2.4. Cell assembly and performance characterization

The electrochemical stability window of the separator was determined by a linear sweep voltammetry experiment at the potential range between 2.5 V and 6.0 V under the scan rate of 1.0 mV · s^{-1} at room temperature [46]. The ionic conductivity of the liquid electrolyte-soaked separator between two stainless-steel plate electrodes was evaluated using the electrochemical impedance spectroscopy (EIS) measurement by applying an AC voltage of 20 mV amplitude in the frequency range of 1 Hz–10^6 Hz [47]. A unit cell (2032-type coin) was composed of a $LiCoO_2$ cathode ($LiCoO_2$/carbon black/PVDF 90/5/5 w/w/w), a natural graphite anode (natural graphite/carbon black/CMC/SBR 93/5/1.25/0.75 w/w/w/w), separator and 1 M $LiPF_6$/EC + DEC (1:1 in volume) electrolyte. All assembly of cells was carried out in an argon-filled glove box. For comparison, cells using the PP separator (Celgard 2500) were assembled and tested under the same condition. The discharge current densities were varied from 0.2 C (24 mA g^{-1}) to 4.0 C (480 mA g^{-1}) under a voltage range between 2.75 V and 4.20 V. The cells were cycled at a fixed charge–discharge current density of 0.5 C/0.5 C for cycle life testing [48].

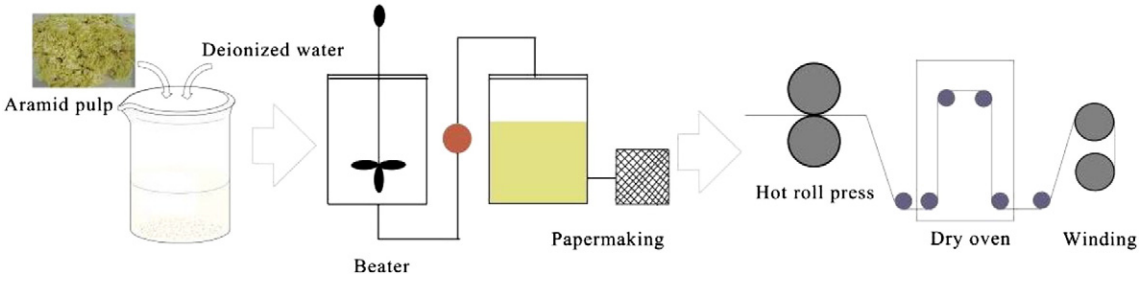

Fig. 1. A schematic illustration for preparation of aramid membrane.