IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

Study on preparation and properties of polyimide lithium battery separator

To cite this article: Haoran Xu *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **493** 012080

Study on preparation and properties of polyimide lithium battery separator

Haoran Xu [1], Meng Li [1], Kai Han [1] and Jijun Xiao [1], Xiaoqi Chen [2], Yantao Li [2, *]

[1] Department of Materials Science and Engineering, Hebei University of Science and Technology, Shijiazhuang, 050000, China
[2] Institute of Energy Source, Hebei Academy of Sciences, Shijiazhuang, 050000, China

*Corresponding author e-mail: 13903116163@163.com

Abstract. Soluble polyimide was synthesized from 4, 4'-(4, 4'-Isopropylidenediphenyl-1, 1'-diyldioxy) dianiline (BAPP), 4, 4'-Diaminodiphenyl ether (ODA) and 4, 4'-Oxydiphthalic anhydride (ODPA) in a certain proportion. The porous polyimide (PI) membranes were prepared by phase transfer method. The molecular structure, pore size, contact angle and thermal stability were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), contact angle measuring instrument. The results show that the prepared porous polyimide membranes have three-dimensional network of microporous structure with a surface pore diameter of 0.5-1 μm; The porosity increases with the increasing quality ratio of anhydrous ethanol and acetone in the solution, which reaches more than twice of the conventional Celgard 2400 membrane;The contact angles of the porous polyimide membranes are smaller than that of separator of the Celgard 2400 membrane and showing better lyophilicity, which were all take distilled water as the test solution. The porous polyimide membranes have better heat resistance, and the size does not change significantly after heat treatment at a maximum of 180℃ for 0.5 h.

1. Introduction

At present, commercial microporous films such as polyethylene (PE) and polypropylene (PP) separators are widely used, but the thermal stability of the separators are poor. For example, the melting point of the polyethylene (PE) membrane is 130°C, and the separator of the battery will melt when it exceeds the melting point. While the melting point of polypropylene (PP) is 163°C, and when the temperature reaches 150°C, the separator shrinkage is nearly 30%, which easily cause safety accident [1-2]. In addition, polyolefins have relatively lower wettability, porosity, and electrolyte absorption rate due to their own chemical structure, resulting in a decrease in battery performance.

Polyimide (PI) refers to a kind of polymer containing the imide group on the main chain. The molecular main chain of this kind of polymer not only contains the five-element ring composed of heteratomic nitrogen, but also contains a very rigid aromatic ring, which is a kind of engineering plastics with high application value. Comparing with polyolefin material, polyimide (PI) has good thermal stability, chemical stability and outstanding mechanical properties [3-5]. Its long-term use temperature can reach up to 300°C, which is the best comprehensive film insulation material [6]. At the same time,

IOP Conf. Series: Materials Science and Engineering **493** (2019) 012080 doi:10.1088/1757-899X/493/1/012080

compared with the polyolefin separator, PI has a good affinity for lithium ion electrolyte due to its polar group, so it is regarded as the next generation lithium ion battery separator material [7-9].

In this experiment, PI was synthesized by one-step method using BAPP, ODA and ODPA as raw materials. The synthesized PI is dissolved in a solvent, and porous polyimide membranes are produced by phase transfer method [10-11]. Compared with traditional polyimide membranes, the heat resistance and contact angle of porous polyimide membranes will change. In this experiment, the porosity, contact angle and heat resistance of porous polyimide membranes were tested and compared with traditional polyolefin membranes, so as to study the applicability of polyimide in battery separator.

2. Experimental

2.1. Materials

4,4'- (4,4'- Isopropylidenediphenyl- 1,1'- diyldioxy) dianiline (BAPP), Changzhou Sunlight Pharmaceutical Co., Ltd; 4,4’- Diaminodiphenyl ether (ODA), 4, 4’- Oxydiphthalic anhydride (ODPA), Changshu Electronic Engineering Compound Material factory; 1 - Methyl- 2- pyrrolidinone (NMP) ; Ethanol absolute, n-Butanol, Benzoic acid, Shanghai Aladdin Bio- Chem Technology Co., LTD; m-Cresol, DAMAO chemical reagent Factory; distilled water, Self-preparation; Celgard 2400. Celgard, US; acetone, Guangzhou Dongsheng Chemical Co., Ltd.

2.2. Characterization

The PI structure was characterized by the US Nicolet is 5 Fourier infrared spectroscopy analyzer.
Japan's S-4800-1 cold field emission scanning electron microscope (SEM) was used to characterize the micropores on the surface of the battery separator. The German KRUSS optical contact angle measuring instrument DSA100 was used, and distilled water was used as a solution to measure the contact angle of the battery separator. The PI separator porosity (P) determination was tested according to the following method:

Cutting a certain area of the film, Weighing its mass to M1, then soak the membrane in n-butanol for 12h, Absorbing surface n-butanol with filter paper, Weighing its mass to M2, The mass of n-butanol absorbed by the microporous membrane is m=M2-M1. The pore volume of the microporous membrane can be obtained by dividing the mass (m) of n-butanol by the density (ρ) of n-butanol.

The porosity calculation formula is:

$$P = \frac{M_2 - M_1}{\rho V}$$

In the formula: V--the volume of the porous PI membrane.

Thermal shrinkage of membrane was determined by measuring the length changes of a 60×60 mm specimen on both machine direction (MD) and transverse direction (TD) after storage in a hot oven at 120°C, 150°C, and 180°C for 0.5h, respectively. The thermal shrinkage was calculated from:

Thermal shrinkage= (Li - Lf) / Li×100wt:%

Where Li and Lf are the initial length and the final length of specimen after high temperature storage, respectively.

2.3. Preparation of porous polyimide membranes

(a) Synthesis of polyimide.

BAPP, ODA and ODPA are dissolved in m-cresol solution at a ratio of 1:1:2 taking benzoic acid as catalyst. The mixture is heated to 180°C under reflux of nitrogen for 12 hours to obtain polyimide solution. Pouring the polyimide solution into 95% ethanol solution to precipitate and wash repeatedly. Then the synthesized polyimide was placed in a vacuum oven at 120°C for 12 h, and stored for use.

(b) Preparation of porous polyimide membranes

Prepare the solutions with acetone, absolute ethanol and NMP at different mass ratio of 0:0:10, 1:1:18 and1:1:8. The 10% PI is respective dissolved in the above three solutions. Then three solutions were prepared and labeled as PI-1, PI-2, PI-3, respectively. Morover, they were poured on clean glass plates, and the films were formed by a film applicator. The prepared membranes were immersed in distilled water for 12 hours, and placed in an environment of 120°C for 4 hours. At last, the membranes named of PI-1, PI-2, and PI-3 were obtained and stored for testing.

3. Results and discussion

3.1. FTIR analysis

It can be seen from the FTIR spectrum of Fig. 1 that 1780 cm-1 and 1720 cm-1 are respectively attributed to the asymmetric and symmetric stretching vibration of C=O; 1380 cm-1 is the C-N vibration peak in the five-membered ring; 725 cm-1 is the C=O bending vibration peak. Thus the significant peak of polyimide characteristics were shown from Fig.1.

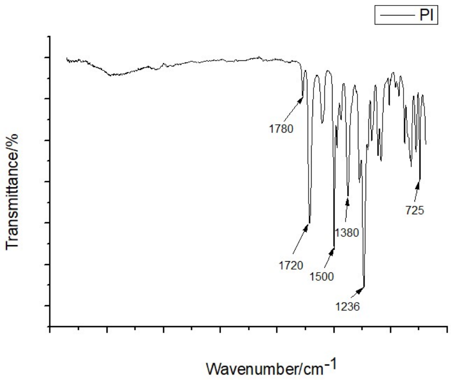

Fig 1. FTIR spectrum of polyimide

3.2. The topography of membranes

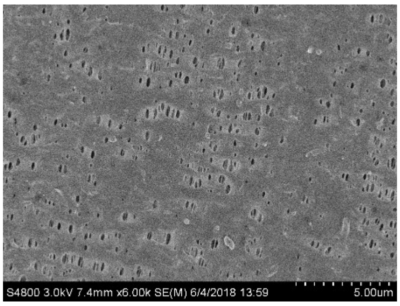

Fig 2. The scanning electron microscope of Celgard 2400 membranes

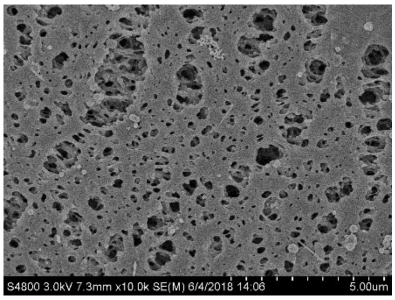

Fig 3. The scanning electron microscope of porous polyimide membranes

Fig. 2 shows a scanning electron microscope of a 6 × 103 times Celgard 2400 membranes, and Fig.3 is of a 1 × 104 times porous polyimide membranes. It can be seen from the figure that the porous polyimide membranes prepared by the phase transfer method has a significantly higher porosity than the Celgard 2400 membranes. The porous polyimide membranes pore size is between 0.5-1 μm and the pores are evenly distributed. The higher porosity for the porous polyimide membranes contributes to the exchange of the electrolyte, which improves the charge and discharge performance of the battery.

3.3. The analysis of porosity

The porosity of the PI-1, PI-2, and PI-3 porous polyimide membranes are shown in the following table 1. It can be seen that the relationship between the three membranes porosity is PI-3> PI-2> PI-1.This is because the porosity of the polyimide membranes can change with the change of the acetone and ethanol absolute content in the solvent, and the porosity can be more than twice that of the traditional polyolefin films. The higher void ratio for the battery separator helps the electrolyte to circulate inside the battery, thereby increasing the charge and discharge efficiency of the battery.

Table 1. Three membranes porosity of PI-1, PI-2 and PI-3

Sample	PI-1	PI-2	PI-3
Porosity	69%	74%	82%

3.4. The analysis of thermal stability

The PI and Celgard 2400 membranes were stored in different temperature for 0.5 h, and the thermal stability of the separator was tested by measuring the change in size before and after measurement. Table 2 shows the dimensional changes of the four separators at different temperatures. At 120 °C and 150°C, the transverse shrinkage of the Celgard 2400 membranes were 13%, 41%, and there were no shrinkage change in the longitudinal direction. What's more, at 180v, the membrane melts and shrinks into small balls.The three porous polyimide membranes have no shrinkage and no deformation at 120 ° C, 150 ° C, 180 ° C for 0.5 h, which has better thermal stability than the traditional Celgard 2400 membranes and effectively improves the safety performance of the lithium ion battery.

Table 2. Thermal shrinkage of PP, PI-1, PI-2 and PI-3 membranes.

Membrane	Shrinkage (%)			
	Direction	120°C	150°C	180°C
Celgard 2400	MD	0	0	Melted
	TD	13%	41%	Melted
PI-1	MD	0	0	0
	TD	0	0	0
PI-2	MD	0	0	0
	TD	0	0	0
PI-3	MD	0	0	0
	TD	0	0	0

3.5. The analysis of contact angle

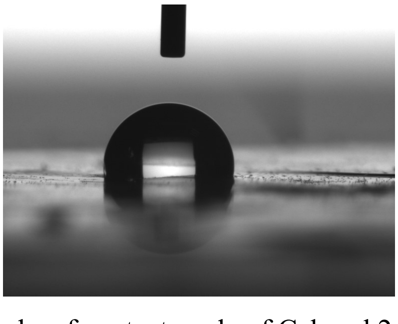

Fig 4. Photographs of contact angle of Celgard 2400 membranes

IOP Conf. Series: Materials Science and Engineering **493** (2019) 012080 doi:10.1088/1757-899X/493/1/012080

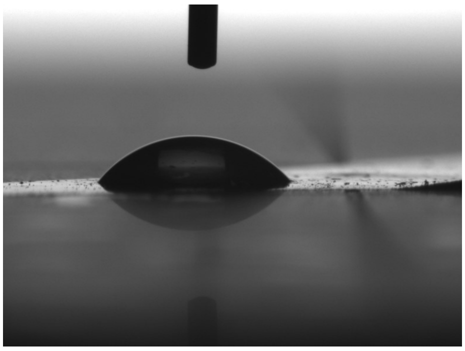

Fig 5. Photographs of contact angle of non-porous PI membranes

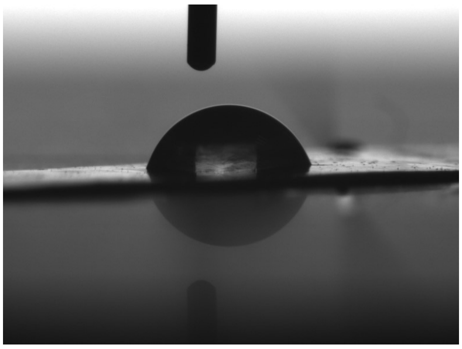

Fig 6. Photographs of contact angle of porous PI membranes

The contact angle of Celgard 2400 membranes > porous PI membranes > non-porous PI membranes from figure.4-6. And table 3 shows the contact angles of the five materials in detail. It is obvious that the contact angle of Celgard 2400 membrane is greater than that of other four porous polyimide membranes. This is because PI has a polar group and has better lyophilicity. By comparison, it can be seen that the contact angle of the porous polyimide membranes gradually increases with the increasing of the porosity, because the lotus effect is formed on the surface of the porous polyimide membranes due to the higher porosity. Thus, porous polyimide membranes exhibit better lyophilic properties than Celgard 2400 membranes.

Table 3. Contact angle of PP, PI-1, PI-2, PI-3 and PI-Nonporous membranes

Sample	PP	PI-1	PI-2	PI-3	PI-Nonporous
Contact angle	100°	70°	75.4°	84.1°	47°

4. Conclusion

The porous polyimide membranes with different porosity were prepared by phase transfer method. The polyimide membranes has a three-dimensional network of microporous structure with a surface pore diameter of 0.5-1 μm. The porosity becomes larger with the increasing ratio of anhydrous ethanol and acetone in the solution, up to 2 times higher than traditional polyolefin battery separator. The contact angle of different porosity polyimide membranes are smaller than that of PP battery separator, showing better lyophilicity. At the same time, the porous polyimide membranes are no significant change through 180° heat treatment for 0.5h and shows better heat resistance. Based on good thermal stability, porosity, and lyophilicity, the porous polyimide membrane is expected to find application in battery separators.

IOP Conf. Series: Materials Science and Engineering **493** (2019) 012080 doi:10.1088/1757-899X/493/1/012080

References

[1] LI X, HE J, WU D, et al. Development of plasma-treated polypropylene nonwoven-based composites for high-performance lithium-ion battery separators [J]. Electrochim Acta, 2015, 167: 396 – 403.
[2] SHAYAPAT J, CHUNG O H, PARK J S. Electrospun polyimide-composite separator for litjium-ion batteries [J]. Electrochim Acta, 2015, 170: 110 – 121.
[3] XIAO Y, LOW B T, HOSSEINI S S, et al. The strategies of molecular architecture and modification of polyimide-based membranes for CO removal from natural gas-A review [J]. Progress in Polymer Science, 2009, 34(6): 561-580.
[4] LIN D, ZHUO D, LIU Y, et al. All-integrated bifunctional separator for Li dendrite detection via novel solution synthesis of a thermostable polyimide separator[J]. Journal of the American Chemical Society, 2016, 138 (34):11044.
[5] LI Z, ZOU H, LIU P. Morphology and properties of po-rous polyimide films prepared through thermally induced phase separation [J]. RSC Advances, 2015, 5(47):37837-37842.
[6] LI J W, ZHANG G C, JING Z X, et al. Synthesis and characterization of porous polyimide films containing benzimidazole moieties [J]. High Performance Polymers, 2017: 869-876.
[7] XIAO J M, SHANG X C, QIN L P. A new route of fabricating porous polyimide membranes [J]. International Journal of Minerals Metallurgy, 2010, 17(6): 782-785.
[8] TIAN Y, LIU S, DING H Y, et al. Formation of deformed honeycomb-patterned films from fluorinated polyimid[J].Polymer,2007,48(8):2338-2344.
[9] YABU H, TANAKA M, IJIRO K, et al. Preparation of honeycomb-patterned polyimide films by self-organization[J].Langmuir,2003,19(15):6297-6300.
[10] NGUYEN T, WANG X. Multifunctional composite membrane based on a highly porous polyimide matrix for direct methanol fuel cells [J]. Journal of Power Sources, 2010, 195(4):1024-1030.
[11] KIM S, JANG K S, CHOI H D, et al. Porous polyimide membranes prepared by wet phase inversion for use in low dielectric applications [J]. International Journal of Molecular Sciences, 2013, 14(5):8698-8707.