



Development of plasma-treated polypropylene nonwoven-based composites for high-performance lithium-ion battery separators



Xiaofei Li, Jinlin He, Dazhao Wu, Mingzu Zhang^{*}, Juwen Meng, Peihong Ni

College of Chemistry, Chemical Engineering and Materials Science, Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Soochow University, Suzhou 215123, PR China

ARTICLE INFO

Article history:

Received 22 December 2014

Received in revised form 24 March 2015

Accepted 26 March 2015

Available online 5 April 2015

Keywords:

lithium-ion battery separators
plasma treatment
polypropylene nonwoven
poly(vinylidene fluoride-co-hexafluoropropylene)

ABSTRACT

Separators have drawn substantial attention because of their important role in achieving the safety and good electrochemical performance of lithium-ion batteries. In this study, we report a new type of composite membrane prepared by a combination of fluorinated polypropylene (PP) nonwoven fabric, poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) and SiO₂ nanoparticles. 2, 2, 3, 3, 4, 4, 5, 5-Octafluoropentyl methacrylate (OFPMA) is first grafted on the surface of PP nonwoven by plasma treatment to improve the nonwoven's adhesion with PVdF-HFP. Two kinds of composite separators have been prepared by using the different PP nonwovens together with PVdF-HFP and SiO₂ nanoparticles. They were separately designated as PHS for commercially raw PP nonwoven system and PHS-n for OFPMA-modified PP nonwoven systems (n means plasma treatment time). The morphology, electrolyte uptake, ionic conductivity and electrochemical properties of the composite separators have been analyzed by scanning electron microscope (SEM) analysis, impedance measurement, charge-discharge cycle and C-rate tests, respectively. The results indicate that PHS-10 composite separator using the modified PP nonwoven treated by plasma for 10 min exhibits much better properties than PHS separator, including an improved mechanical property, thermal stability, electrolyte uptake (290 wt%) and ionic conductivity (1.76 mS cm⁻¹). More importantly, the LiFePO₄/Li half-cell assembled with PHS-10 composite separator displays a good C-rate performance, which shows an enhancement in the chemical stability and discharge capacity. The capacity keeps above 150 mAh g⁻¹ after 100 charge-discharge cycles. These performances endow this composite membrane as a promising candidate for high-performance lithium-ion battery separators.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

With fossil fuel energy decreasing and green renewable resources developing, the energy storage and conversion devices will play an increasingly significant role in the future. As an important representative of the class, lithium-ion batteries (LIBs) have been widely used in portable electronic devices, as well as some emerging fields including low emission vehicles and long-term energy storage systems due to their high specific energy, low self-discharge rate and long cycling lifetime [1–4]. In general, a lithium-ion cell is mainly comprised of positive and negative electrodes, separator and electrolyte. Among various components, the separator plays a key role to retain electrolyte, prevent electrical short circuit between electrodes and allow the rapid transport of ionic charge carriers [5,6]. The property of separator

has great influence on the internal resistance, charge-discharge process, capacity and safety of LIBs [7].

Currently, microporous polyolefin membranes have been broadly applied as the separators in the commercial LIBs mostly because of their comprehensive performances [6,7]. However, there are still some disadvantages including insufficient wettability, poor thermal resistance and low liquid electrolyte retention, which can lead to some potential safety issues and can not meet the requirements of wide use in energy storage devices. Hence, much efforts have been done to overcome these drawbacks, such as the modification of polyolefin separator [8–10], preparation of composite separator [11–15] and development of new materials used for separator [16–22].

With the increasing safety demands on the LIBs, much more attentions have been paid on gel polymer electrolytes (GPEs), which possess a three-dimension structure, as well as the improved ionic conductivity and liquid electrolyte retention [23,24]. However, the mechanical properties of GPEs are usually poor and this is one of the main deficiencies that hindered them to be

^{*} Corresponding author.

E-mail address: zhangmingzu@suda.edu.cn (M. Zhang).

used in practical batteries. Several strategies have been proposed to solve this problem, among which the surface coating of commercial polyolefin separators or nonwoven fabrics to prepare the composite separators is one of the promising approaches [25–27]. For example, Kim et al. reported a porous polyethylene (PE) separator coated with acrylonitrile-methyl methacrylate copolymer and obtained a composite separator with satisfactory performances [28]. In our recent studies [15,26], we have also prepared composite separators based on PP nonwoven fabrics and SiO₂ nanoparticles to improve the physical and electrochemical performances, as well as reduce the production cost.

Although the mechanical properties of the composite separators could be improved by the incorporation of surface coatings, the composite process would produce new interfacial resistance between the support membrane and coating materials, thus resulting in lower ionic conductivity and reduced cell performance. However, this issue was rarely considered. Therefore, in order to reduce the interfacial resistance and improve the ionic conductivity of the composite separators, it is necessary to modify the surface of support frames and increase the interfacial compatibility. For instance, Kim's group modified PE separator by using gamma ray irradiation and found that the irradiated separator showed stronger affinity for polar solvents and enhanced properties compared with the unirradiated separator [25]. Several techniques have been used for modification of the separators, such as exposure to electron beam [8], gamma ray irradiation [25], UV light [29] and plasma irradiation [30,31]. Among them, plasma treatment exhibits unique advantages including environment-friendly process, low production cost and easy commercialization. In particular, this method only changes the upper molecular layers on the surface of matrix, but not affects the bulk properties of the polymers [32].

Herein, we report on the preparation and characterization of a new composite separator which is composed of PP nonwoven fabric grafted with fluorinated polymer by plasma treatment, PVdF-HFP and SiO₂ nanoparticles. PP nonwoven fabric was used as the support material due to its favorable mechanical strength and relatively low cost [5,7]; PVdF-HFP was selected as the polymer film because of its low crystallinity, high dielectric constant and excellent chemical stability [4–7]; SiO₂ nanoparticles were doped in the polymer matrix since it has been reported that nanosized inorganic particles such as aluminum oxide (Al₂O₃), silicon dioxide (SiO₂) and titanium dioxide (TiO₂) can significantly improve the mechanical strength, thermal stability and ionic conductivity of polymer electrolytes [7,14,15]. In addition, in order to improve the interfacial compatibility, PP nonwoven was first treated by plasma treatment in the presence of 2, 2, 3, 3, 4, 4, 5, 5-octafluoropentyl methacrylate (OFPPMA) for different time. The buffer layer was formed from the fluorinated segments immobilized on the surface

of PP, which improved the adhesion between PP and PVdF-HFP, and further increased the ionic conductivity of the composite separator. The main purpose of this research is to improve the mechanical property, ionic conductivity and cell performance of composite separator, and finally to fabricate a high-performance composite separator for LIBs.

2. Experimental

2.1. Materials and chemicals

Commercially raw PP nonwoven fabric (Changxing Tianchuan Nonwovens Co., $\rho = 9 \text{ g m}^{-2}$) was first presoaked and then washed with acetone to remove any chemicals adsorbed on the surface, and finally dried under vacuum at room temperature till a constant weight. 2, 2, 3, 3, 4, 4, 5, 5-Octafluoropentyl methacrylate (OFPPMA, TCI), poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP, Solvay), poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (Pluronic F127, Sigma-Aldrich), Celgard[®] monolayer PP separators (2400, Celgard LLC), LiFePO₄ (Heolo Technology) and lithium tablet (China Energy Lithium) were used as received. Silica nanoparticles (SiO₂, the average diameter (\bar{D}_z) is about 20 nm, Hangzhou Wanjing New Material Technology) were dried at 120 °C overnight in a vacuum oven prior to use. The liquid electrolyte solution consisting of 1.0 mol L⁻¹ lithium hexafluorophosphate (LiPF₆) and the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v) was obtained from Zhangjiagang Guotai-Huarong New Chemical Materials. Other reagents were purchased from Shanghai Chemical Reagent and used as received.

2.2. Grafting of OFPPMA on the surface of PP nonwovens by plasma treatment

The plasma treatment system (Suzhou OPS Plasma Technology) is composed of four main parts: one tubular-type Pyrex reactor ($\Phi 16 \text{ cm} \times 21 \text{ cm}$) equipped with several inner electrodes, one vacuum pump, one gasification grafting instrument, as well as one radio-frequency (RF) power supply and control system. PP nonwovens were placed between two paralleled copper electrodes and OFPPMA was heated to 80 °C by the gasification grafting instrument. Subsequently, the plasma reactor chamber was evacuated to a high vacuum and the plasma gas was then introduced. The applied RF power was fixed at a relatively low value (80 W) to minimize the plasma-induced surface etching, while the plasma gas in the chamber was kept at 30 Pa by a pressure regulator. After that, plasma was generated for different time (5, 10, 15 and 20 min, respectively) to treat the PP nonwovens. Finally, the treated PP nonwovens were taken out and washed with acetone to remove the possible polymer fragments and other

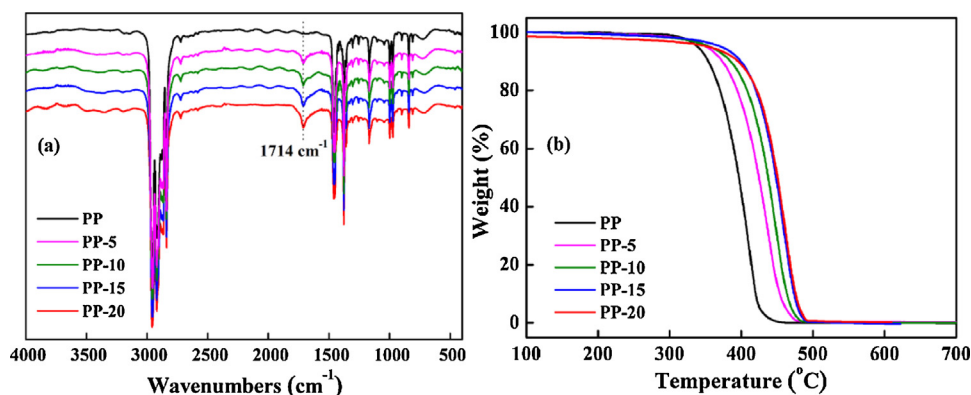


Fig. 1. (a) FT-IR spectra and (b) TGA curves of commercial PP and OFPPMA-grafted PP-n nonwovens, where n represents the plasma treatment time.

Download English Version:

<https://daneshyari.com/en/article/184367>

Download Persian Version:

<https://daneshyari.com/article/184367>

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