Journal of Power Sources 271 (2014) 134–142

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Sandwich-like heat-resistance composite separators with tunable pore structure for high power high safety lithium ion batteries

Junli Shi, Tao Shen, Huasheng Hu, Yonggao Xia*, Zhaoping Liu*

Ningbo Institute of Materials Technology Engineering (NIMTE), Chinese Academy of Sciences, Zhejiang 31520, PR China

HIGHLIGHTS

- Separators with a unique sandwich-like structure are developed.
- Excellent thermal stability and flame retardant ability contribute to higher battery safety.
- Separators exhibit superior cell performances than commercial PP separator.
- New insight into the influences of separators on the cell performances is proposed.

ARTICLE INFO

Article history:
Received 4 June 2014
Received in revised form
19 July 2014
Accepted 22 July 2014
Available online 4 August 2014

Keywords:
Lithium ion battery
Nonwoven
Composite separator
Crosslink
Safety

ABSTRACT

We demonstrate a new kind of composite separators. A unique feature of the separators is the three-tier structure, i.e. the crosslinked polyethylene glycol (PEG) skin layer being formed on both sides of the nonwoven separators by in-situ polymerization and the large pores in the interior of the nonwoven separators being remained. The surface pore structure and the thickness of the skin layer could be adjusted by controlling the concentration of the coating solution. The skin layer is proved to be able to provide internal short circuit protection, to contribute a more stable interfacial resistance and to alleviate liquid electrolyte leakage effectively, yielding an excellent cyclability. The remained large pores in the interior of the composite separators could provide an access for the fast transportation of lithium ions, giving rise to a very high ion conductivity. The polyimide (PI) nonwoven is employed to ensure enhanced thermal stability of the composite separators. More notably, the composite separators fabricated from the coating solution with a composition ratio of 20 wt% provide superior cell performances owing to the well-tailored microporous structure, comparing with the commercialized polypropylene (PP) separator, which show great promise for the application in the high power lithium ion batteries.

1. Introduction

The expanding applications, including (hydrid) electric vehicles and energy storage systems, have put forward higher requirements for lithium ion batteries [1,2]. High energy/power density, high-security have been an important developing trend [3]. Accordingly, the performances of the battery components, including cathode, anode and separator, are urgently needed to be improved. Thereinto, separator plays an important role in preventing the physical contact between the electrodes, retaining liquid electrolyte and conducting lithium ions. These features of the separator would largely influence battery safety and power density [4]. Currently, polyolefin based separators are widely used in commercialized lithium ion batteries due to their low price and chemical durability. However, their poor thermal stability and poor wettability have raised serious concerns on their capacity for the application in high power lithium ion batteries [5].

Various efforts have been done to overcome the drawbacks of polyolefin based separators, for example, introducing the inorganic or organic coating layer to enhance the thermal resistance and wettability [6,7]. Recently, heat-resistance nonwoven separators have also been developed [8,9]. The high porosity and excellent thermal properties have attracted considerable attention. This kind of separators is typically manufactured from heat-resistance engineering polymer, such as polyester (PET) [9], polyimide (PI) [10], polyacrylonitrile (PAN) [11] and so on, which usually own higher

---

* Corresponding authors. Tel./fax: +86 574 86685701.
E-mail addresses: xiayg@nimte.ac.cn (Y. Xia), liuzp@nimte.ac.cn (Z. Liu).

http://dx.doi.org/10.1016/j.jpowsour.2014.07.151
0378-7753/© 2014 Elsevier B.V. All rights reserved.

melting temperature (>250 °C) than the traditional polyolefin based separators. When this kind of nonwoven separators is deposited at a high temperature (for instance, 180 °C), they could still keep the initial dimension steadily and could effectively avoid short circuit between the electrodes. So the nonwoven separators are now deemed as an important candidate for separators used in high power lithium ion batteries. However, the excessively large pore size and relatively weak interaction with liquid electrolyte usually cause internal short circuit, overgrowth of lithium dendrite, self-discharge and electrolyte leakage, which would further deteriorate the battery cycle performances and safety [5].

To resolve the limitations of the nonwoven separators, Zhu et al. [2] prepared a kind of poly(vinylidene fluoride) (PVDF) gel polymer electrolyte doped nonwoven separator. The gel part could effectively prevent liquid electrolyte leakage and provide a more intimate contact with the electrodes to enhance the interfacial stability [2]. However, the fully populated pores are not conducive to the rapid diffusion of the lithium ions, which might further restrict the improvement of battery power performances. Lee et al. [12–15] developed various kinds of colloidal particle and inorganic nanoparticle composite nonwoven separators. The introduction of the particles helped to decrease the pore size of the nonwoven substrate. Meanwhile, the well-connected interstitial voids between the particles could provide an easy access for liquid electrolyte penetration and lithium ion transportation. But they have also pointed out that long-term durability of this kind of composite nonwoven separators, especially for the colloidal particle embedded nonwoven separator, still needs more considerations. [13] To effectively avoid the shortcomings of large pores on the surface, at the same time to play the advantage of the high porosity of the nonwoven separator and to provide a more stable modification layer, a new kind of sandwich-like composite separator (Fig. 1) was designed in this work. Crosslinked polyethylene glycol (PEG) layer was introduced onto both sides of the nonwoven separator by in situ polymerization, which could firmly lock the surface nonwoven fabric and further improve the long-term durability of the composite separator. The surface pore size could also be effectively decreased, which could alleviate liquid electrolyte leakage and restrict the growth of lithium dendrite. [16] The remained large pores in the interior of the composite separator were expected to provide quick access for lithium ion and to make contribution for the superior rate capability of lithium ion batteries. The content of the crosslinked PEG was changed, and the morphology changes and electrochemical performances of the composite separators were explored.

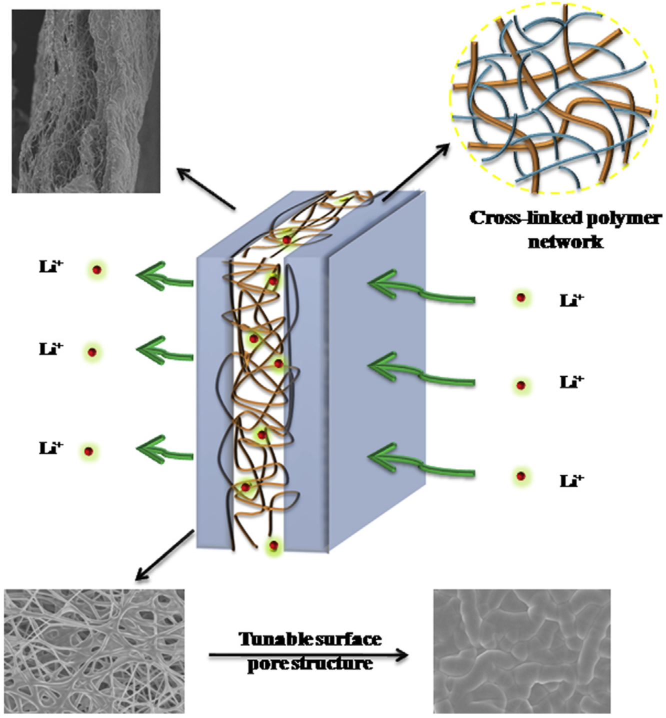

Fig. 1. Schematic principle of the sandwich-like composite separator for lithium ion batteries.

2. Experimental

2.1. Materials

Polypropylene (PP) separator with 42% porosity (20 μm) was bought from Donghang Optoelectronics Technology Co., Ltd., China. PI nonwoven substrate was kindly provided by Jiangxi Xiancai Science and Technology Co., Ltd., China. The thickness is 38 μm, and the porosity is about 80%. Poly(ethylene glycol) methyl ether acrylate (PEGMEA, *Mn* = 700) and Poly(ethylene glycol diacry) (PEGDA, *Mn* = 700) were supplied by Aladdin Reagent Company. 2, 2′-Azobis (2-methylpropionitrile) (AIBN) and acetone were obtained from Sinopharm Chemical Reagent Co., Ltd, China. PEGMEA, PEGDA and AIBN were purified before use. The electrolyte solution of $LiPF_6$ (1 mol L^{-1}, SZ-SSDE-NIM-006, ion conductivity 10^{-2} S cm^{-1} at 25 °C) was provided by BASF Battery Materials (Suzhou) Co. Ltd., China.

2.2. Preparation of the sandwich-like composite separators

Proportional PEGMEA, PEGDA and AIBN were added in acetone and were then stirred to be homogenous at room temperature. The composition of the mixed coating solution was shown in Table 1. The monomer solution impregnated non-woven fabric was obtained by a traditional dip-coating method. The nonwoven substrate was immersed in the monomer solution for 2 min and was then draw out through a slit (45 μm) to remove redundant solution. The obtained film was heated at 60 °C in the oven for 6 h. In this process, a free-radical addition reaction between PEGMEA and PEGDA would happen, and the crosslinked PEG skin layer would be formed on both sides of the nonwoven substrate. Solvent evaporation would take place simultaneously. A series of sandwich-like composite separators were finally achieved. The corresponding codes are listed in Table 1.

2.3. Characterizations of the sandwich-like composite separators

The SEM photographs were obtained by field emission scanning electron microscopy (FESEM) (S-4800, Hitachi) after samples were coated by gold. Gurley value (sec 100 cc^{-1}) was achieved by

Table 1
Composition of the monomer solutions and the corresponding code of the composite separators.

Code	Solution composition				Monomer concentration (wt%)	Thickness (μm)
	PEGMEA (g)	PEGDA (g)	AIBN (g)	Acetone (g)		
A	0.00	0.00	0.00	0.00	0	38.0
B	0.80	0.20	0.018	9.00	10	39.9
C	1.60	0.40	0.020	8.00	20	40.6
D	1.80	0.45	0.022	5.25	30	42.2
e	2.40	0.60	0.024	4.50	40	42.8