Journal of Power Sources 400 (2018) 502–510

Contents lists available at ScienceDirect

Journal of Power Sources

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

Highly safe lithium-ion batteries: High strength separator from polyformaldehyde/cellulose nanofibers blend

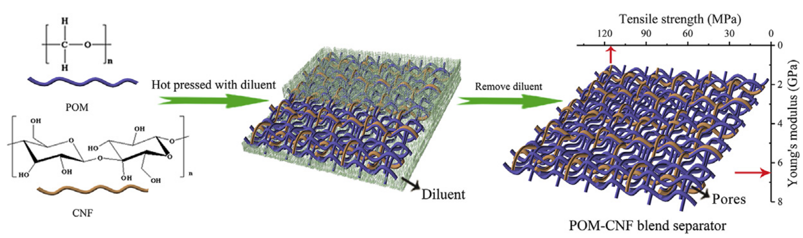
Junchen Liu, Kai Yang, Yudi Mo, Shuanjin Wang, Dongmei Han, Min Xiao**, Yuezhong Meng*

The Key Laboratory of Low-carbon Chemistry & Energy Conservation of Guangdong Province, State Key Laboratory of Optoelectronic Materials Technologies, Sun Yat-sen University, Guangzhou 510275, PR China

HIGHLIGHTS

- This is a first report about polyformaldehyde/cellulose blend separator.
- The blend separator shows high porosity of 78% and good electrolyte wettability.
- High ionic conductivity of 1.39 mS cm-1 and lower interface resistance of 49.5 Ω.
- Outstanding tensile strength of 116 MPa and very high Young's modulus of 6.07 GPa.
- The cell with blend separator shows 0.059% capacity fading per cycle at 200 mA g-1.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Membrane
Lithium ion batteries
Separator
Polyformaldehyde
Cellulose nanofibers
Thermally induced phase separation

ABSTRACT

As a pivotal part of lithium-ion batteries, separator is supposed to have high strength, thermal stability and excellent wettability. In this study, polyformaldehyde/cellulose nanofibers blend separators are firstly prepared via thermally induced phase separation to improve the performance, especially the safety of LIBs. The polyformaldehyde/cellulose blend separators show considerable tensile strength (116 MPa) and Young's modulus (6.07 GPa) owing to the high crystallinity and high performance of polyformaldehyde and cellulose. In particular, benefiting from their abundant polar groups and highly porous structure, the polyformaldehyde/cellulose blend separators possess high electrolyte uptake (412%) and small contact angle (19°) as compare to the commercial polyethylene separator (115%, 58°). Moreover, the thermal treatment tests indicate that the polyformaldehyde/cellulose blend separators are thermally stable at as high temperature as 180 °C. And the polyformaldehyde/cellulose blend separators show higher ionic conductivity (1.39 mS cm^{-1}) and lower interface resistance (49.5 Ω) than polyethylene separator (0.76 mS cm^{-1}, 136.4Ω). As expected, the $LiFePO_4$/Li cell with polyformaldehyde-20-cellulose blend separators exhibit the best stable cycling performance and improved rate performance than PE separator, especially at high rate. In summary, the polyformaldehyde/cellulose blend separators are promising new kind of separator for LIBs with high safety and enhanced performance.

* Corresponding author.
** Corresponding author.
E-mail addresses: stsxm@mail.sysu.edu.cn (M. Xiao), mengyzh@mail.sysu.edu.cn (Y. Meng).

https://doi.org/10.1016/j.jpowsour.2018.08.043
Received 12 June 2018; Received in revised form 6 August 2018; Accepted 13 August 2018

1. Introduction

Lithium-ion batteries (LIBs) have always been an effective solution for energy crisis and environment pollution owing to their high energy density, long cycle life, environmental friendliness and portability [1–3]. Nowadays, LIBs are widely used not only in portable electronic, but also in electric vehicles [4,5], which promote requirements of safe and cheaper LIBs with high energy density and charge/discharge rate performance [6–8]. The separator plays a vital role of insulating cathode and anode as well as allowing the transportation of lithium ion between the electrodes [9,10]. The robust mechanical strength and thermal stability of separator are the basic guarantee for safety of the LIBs [11–13]. Meanwhile, high porosity and electrolyte wettability are necessary for high electrochemical performance of the LIBs [14,15].

So far, the commercial separators for LIBs are generally based on polyolefin separators, such as polyethylene (PE), polypropylene (PP) and their composite because of their good chemical stability, desirable mechanical strength and low cost [16]. However, there are some inherent drawbacks of the polyolefin separators, such as low porosity, inferior electrolyte wettability and unsatisfactory thermal stability at elevated temperatures, which seriously impedes the electrochemical and safe performance of LIBs [17,18]. Therefore, it is urgent need of exploiting an alternative separator for high performance LIBs.

Up to now, many efforts have been adopted to solve aforementioned issues [19–21]. For example, introducing inorganic materials (such as SiO_2 [22–24], CeO_2 [25], ZrO_2 [26], TiO_2 [27] and Al_2O_3 [28–30]) to polymer-based separators could enhance the thermal stability and wettability of the composite separators. Unfortunately, the inorganic particles are usually easy to shed from separators and influence LIBs performance, especially at elevated temperature [31,32]. In addition, replacing the polyolefin with other polymers with higher heat-resistant and mechanical strength can also be an effective solution, such as poly (vinylidene fluoride) (PVDF) [33,34], polyimide (PI) [35,36], poly (ethylene terephthalate) (PET) [37,38], poly (m-phenylene isophthalamide) (PMIA) [39,40] and cellulose-based composite separator [41–43]. Cellulose is one of the most abundant, low cost and renewable polymer. Recently, cellulose-based materials have been employed as separators of LIBs due to their outstanding electrolyte wettability, excellent thermal stability and mechanical properties [44].

Polyformaldehyde (POM) is a kind of high crystalline polymer, which known for its excellent mechanical strength, thermal and chemical stability [45]. In addition, POM is supposed to have strong interaction with carbonate electrolyte of LIBs due to the fact that the polar oxygen atoms in its backbone. What's more, it is worth noting that the cost of POM polymer is relatively low [46]. These above advantages promote POM to be a potential alternative material for LIBs separator. Nevertheless, the poor solubility of POM as its extreme stability limits its application in separator filed. In other word, the POM separator is difficult to be prepared by usual non-solvent induced phase separation (NIPS) [35] or electrospinning [15,35]. Recently, a few studies were focused on the preparation of porous separators via thermally induced phase separation (TIPS) [47,48], which is suitable for preparing porous separators from semi-crystalline thermoplastic. Comparing with other separator preparation techniques, TIPS is more reliable for controlling the pore structure. Besides, the separators prepared via TIPS show higher porosity, more uniform porous structures and higher mechanical strength [49].

In this study, we first report the strategy to combine the advantage of POM and cellulose nanofibers (CNF) and prepare POM-CNF blend separators via TIPS for high performance LIBs (Fig. 1). Besides, we investigated the effect of POM/diluent ratio in the precursor blends on the structure and properties of the resultant separators and performance of LIBs employing these separators. The POM-CNF blend separators have the synergistic advantages of POM and CNF, which exhibit significantly better mechanical strength, electrolyte wettability, thermal stability and LIBs performance when compared with commercial PE separator.

2. Experimental

2.1. Materials

Polyformaldehyde (POM, C9021, $\rho = 1.41\ g\ cm^{-3}$, $M_W = 170000\ g\ mol^{-1}$) was purchased from Celanese Co. Ltd. (America). Cellulose nanofibers (CNF, diameter: 5–50 nm, length: ≥1 μm) were purchased from Zhongshan Nanofiber New Material Co. Ltd. (China). Diphenyl ketone (DPK, analytical reagent grade) was purchased from Aladdin Co. Ltd. (Shanghai, China). Chloroform was purchased from Guangzhou Chemical Reagent Factory (China). The liquid electrolyte was purchased from DoDoChem (Suzhou, China), which consisted of $1\ mol\ L^{-1}$ $LiPF_6$ in the mixture of dimethyl carbonate, diethyl carbonate and ethylene carbonate (1:1:1, volume ratio), referred to as "electrolyte" hereinafter unless specified otherwise. All reagents were purchased commercial and used without future purification. PE separator prepared by wet-method was purchased from Asahi KASEI (Japan) as commercialized separator.

2.2. Preparation of POM-CNF blend separators

The POM-CNF blend separators were prepared via TIPS methodology and DPK was used as the diluent [50]. The weight ratio of POM/CNF was fixed at 95/5, and the weight ratios of POM/DPK were 15/85, 20/80, 25/75 and 30/70. POM, CNF and diluent were mixed at 180 °C with vigorous stirring for 4 h under nitrogen atmosphere to form a homogeneous solution. The POM/CNF/diluent solution was quenched in liquid nitrogen to solidify followed by chopping into power. Then a uniform film was formed through hot calendaring in a mold with vulcanizing press at 180 °C, 4 MPa. After immersing the film in chloroform for 24 h to extract diluent, the prepared separators were dried in vacuum oven at 50 °C for 12 h. According to the different weight ratio of POM/diluent, the prepared POM-CNF blend separators are named POM-15-CNF, POM-20-CNF, POM-25-CNF and POM-30-CNF separately. The number indicates the percentage of POM used.

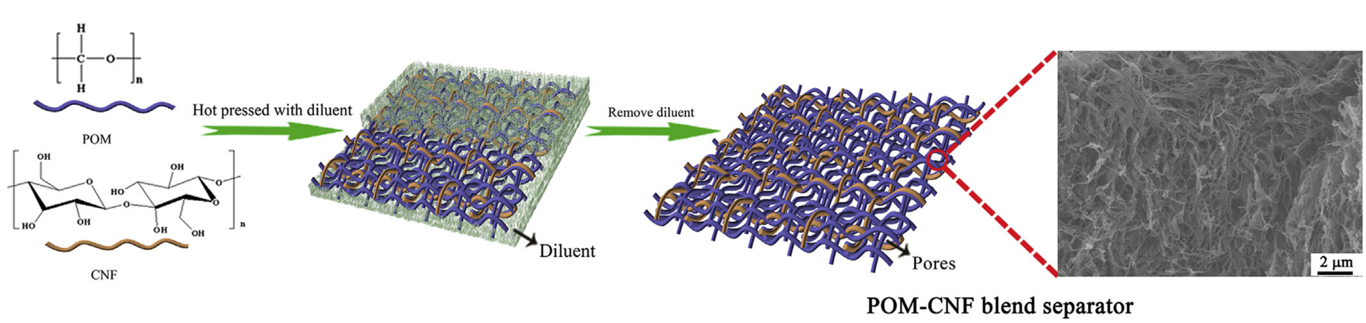


Fig. 1. Schematic illustration of the preparative procedure of POM-CNF blend separator.