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Polypropylene/polyethylene multilayer separators with enhanced thermal stability for lithium-ion battery via multilayer coextrusion

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ABSTRACT

A facile and continuous method to prepare porous polypropylene (PP)/polyethylene (PE) multilayer membranes as separators for lithium-ion batteries via multilayer coextrusion and $CaCO_3$ template method is proposed. Scanning electron microscopy (SEM) images indicate that the membrane exhibits abundant and well-connected sub-micron porous structure. Besides, the physical and electrochemical properties of the membranes, such as thickness, porosity, electrolyte uptake, ionic conductivity, electrochemical stability, thermal stability, and battery performance, are characterized and compared with the commercial separators with trilayer construction of PP and PE (e.g., Celgard® 2325). The results indicate that the multilayer PP/PE separators exhibit higher porosity as well as higher electrolyte uptake and retention than Celgard® 2325, which will definitely increase the ionic conductivity, and consequently improve the battery performances. More importantly, the PP/PE multilayer separators not only show effective thermal shutdown function, but also shows significant advantages of high thermal stability up to 160 °C. The thermal shutdown function of PP/PE multilayer membranes can be adjusted widely in the temperature range from 127 °C to 165 °C, which is wider than that of the commercial separators. The above results combined with the convenient and cost-effective preparation process makes porous PP/PE multilayer membranes a promising alternative to the commercialized trilayer lithium-ion battery separators.

1. Introduction

Lithium-ion batteries (LIBs) have been predominantly used in portable consumer electronics due to their high specific energy density, long cycle life, and lack of memory effect [1,2]. Furthermore, LIBs are also regarded as one of the most promising power sources for electric vehicles and aerospace systems [3,4]. However, the improvements in safety are still urgently required for full acceptance of LIBs in these newly growing application fields. The presence of the combustible electrolyte, as well as the oxidant (lithium oxide cathodes) makes LIBs susceptible to fires and explosions [5]. Once LIBs are subjected to extreme conditions such as short-circuiting, overcharging, and high-temperature thermal impacting [6], the exothermic chemical reactions will be initiated between the electrodes and the electrolyte, which will raise the internal pressure and temperature of the battery [7]. The increased temperature will accelerate these reactions and release heat rapidly through the dangerous positive feedback mechanism, which will lead to thermal runaway [8], cell cracking, fire or even explosion [9]. During the past two decades, there were more than 100 battery-related air incidents involving fire, extreme heat, or explosion according to Federal Aviation Administration (FAA) [5]. To prevent catastrophic thermal failure in LIBs, plenty of strategies including temperature-sensitive electrode materials [10], positive temperature-coefficient electrodes [11], and thermal shutdown electrodes [6,12] have been proposed as a self-activating protection mechanism to prevent LIBs from thermal runaway. While the above methods often involve in either difficult material synthesis or complicated electrode processing, which make them inconvenient for battery application. Besides, the thick coating layers of the electrodes would decrease the energy density of the batteries and hinder their practical use in batteries. From the viewpoint of industrial application, the thermal shutdown separator is therefore the most attractive means for safety protection of LIBs since it can overcome the above defects [6].

Shutdown separators rely on a phase change mechanism to limit ionic transport via formation of an ion-impermeable layer between

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the electrodes [13]. Shutdown separators typically consist of polypropylene (PP)/polyethylene (PE) bilayer or PP/PE/PP trilayer structure. In such kind of laminated separators, PE with lower melting point serves as shutdown agent while PP with higher melting point serves as mechanical support [14]. Once the internal temperature rises up to the melting point of PE, the PE layer is softened and melted to close off the inner pores and thereby preventing ionic conduction and terminating the electrochemical reaction [5]. The majority of the commercial bilayer or trilayer separators are made by laminating different functional layers together by calendaring, adhesion, or welding. The traditional method of making such bilayer or trilayer separators comprises the procedure of making the microporous reinforcing layer and shutdown layer by the stretching process, bonding the above microporous layers alternately into the bilayer or trilayer membranes. Afterwards, the bilayer or trilayer membranes were stretched to the bilayer or trilayer battery separator with required thickness and porosity [15–17]. In addition, other methods to fabricate the multilayer separators have been reported in patent literature. For example, Tabatabaei et al. investigated the fabrication of microporous polypropylene/high density polyethylene/polypropylene trilayer membranes as well as monolayer films using the cast extrusion followed by stretching. The results indicate that the tensile properties and the puncture resistance were improved. Besides, the trilayer membranes showed a lower permeability than the monolayer membranes due to the presence of the interface [18]. Callahan et al. described a fabrication process for multilayer separators including the steps of preparing a film precursor by blown film extrusion, annealing the film precursor and stretching the annealed film precursor to form the microporous membrane [19]. The above methods can produce multilayer separators with thermal shutdown function, and most of which include the stretching process and obviously enhance the mechanical strength of separators. Nevertheless, the quite cumbersome production process clearly decreases the production efficiency. Furthermore, the stretching process has high requirements for the equipment, which will increase the production cost. More importantly, these separators will suffer significant shrinkage from rather limited temperature range, with an onset for shrinkage around 100 °C because of the residual stresses induced during the stretching process of the separators and the difference in density between the crystalline and amorphous phases of the separator materials [13,20], where a potential internal shorting of the cell could occur [21].

To improve the thermal stability of the current polyolefin separators, various surface modification approaches have been devoted to minimize the shrinkage of separators. For example, the dip-coating of some organic polymers or inorganic oxides with excellent thermal stability onto the surface of the polyolefin separators has been extensively studied [22–25]. Although layer coated separator shows significantly improved thermal stability, the coated layer are easy to fall off when the separator is bent or scratched during the battery assembly process [26]. Moreover, the dip-coating method also generates inevitable negative effects, such as the seriously blocked porous structure [23], unmodified inner pores of separators, as well as the significantly increased thickness [13,21,25], which is unfavorable for the cell electrochemical performance [27]. Besides, constructing the heat-resistant skeleton can also solve the thermal shrinkage issues, such as cellulose based composite nonwoven separator [28], porous polyether imide separator [29], and polymethyl methacrylate colloidal particles-embedded poly(ethylene terephthalate) composite nonwoven separator [30]. Even though the above-mentioned separators exhibit improved thermal stability, the complicated manufacturing process makes the separators more expensive [31]. It is essential to find new methods which can optimize the thermal stability, shutdown property and electrochemical performance of polyolefin separators without sacrificing their excellent microporous structure and low-cost.

In the present study, a novel strategy is proposed to prepare multilayer LIB separators comprising alternated layers of microporous PP layer and PE layer via multilayer coextrusion combined with $CaCO_3$ template method. This approach combines the advantages of the multilayer coextrusion (continuous process, economic pathway for large-scale fabrication, and tunable layer structures) and the template method (simple preparation process and tunable pore structure). A key improvement of this approach is that the porous structure is formed by the template method instead of the stretching process, which is beneficial for the thermal stability. Compared to the commercial bilayer or trilayer separators, the dimensional shrinkage of these multilayer membranes may be reduced. More significantly, this approach is quite convenient and efficient, avoid the traditional bilayer or trilayer cumbersome processes during the production process. Physical and electrochemical properties as well as morphology of the separators are studied systematically. Such novel multilayer separators may possess three-dimensional interconnected porous structure and ideal thermal shutdown function, exhibit higher ionic conductivity, better battery performance, wider electrochemical window and shutdown temperature window than commercial separators. The above advantages make this membrane a promising candidate for the application as high performance LIBs separators. Moreover, this method is applicable to any melt-processable polymer in addition to PP and PE.

2. Experimental

2.1. Materials

Polypropylene (PP, V30G) and polyethylene (PE, Q210) resin (injection and extrusion grade) were purchased from Sinopec Shanghai Petrochemical Co.. $CaCO_3$ particles (diameter 0.1 μm) were purchased from Changxing Huayang Sujia Co.. Hydrochloric acid (AR grade, 36.0–38.0%) was purchased from Sinopharm Chem. Reagent Co.. Isopropyl dioleic (dioctylphosphate) titanate (TMC 101) was obtained from Tianchang Green Chem. Additive Factory. Cationic dyeing agent (turquoise blue X-GB) was purchased from Guangzhou Rongqing Chem. Products Co.. The commercialized PP/PE/PP separator (Celgard® 2325) and commercialized PE separator (SK Energy) were selected as the control sample. Prior to the processing, PP, PE, and $CaCO_3$ particles were dried separately at 70 °C for 48 h in vacuum oven to remove any humidity which may have been adsorbed during storage. The lithium-ion electrolyte (1.0 M $LiPF_6$ in ethyl methyl carbonate (EMC)/ethylene carbonate (EC)/dimethyl carbonate (DMC) with the volume ratio of 1:1:1) used in this study was purchased from Shenzhen Tiancheng Technology Co..

2.2. Preparation of porous PP/PE multilayer membranes

The porous PP/PE multilayer membranes were prepared via the combination of multilayer coextrusion and $CaCO_3$ template method. The preparation steps are as follows, (1) Preparation of PP ($CaCO_3$) and PE ($CaCO_3$) masterbatches. Prior to the multilayer coextrusion, $CaCO_3$ particles were pre-dispersed in PP or PE resins with TMC 101 as dispersing agent. $CaCO_3$ particles and PP (or PE) resins with the mass ratio of 66: 34 were mixed and put into the twin-screw extruder to prepare PP ($CaCO_3$) or PE ($CaCO_3$) masterbatches. (2) Preparation of porous PP/PE multilayer membranes. The schematic representation of the lab self-designed multilayer