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Facile fabrication of multilayer separators for lithium-ion battery via multilayer coextrusion and thermal induced phase separation

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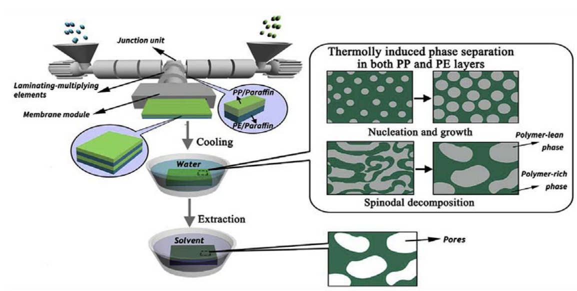
HIGHLIGHTS

- A continuous method to fabricate multilayer separators for Li^+ battery is proposed.
- The method compose of multilayer coextrusion and thermal induced phase separation.
- The method has no stretching process and can avoid the large dimensional shrinkage.
- The separators have better thermal stability and wider shutdown temperature window.
- The separators exhibit higher porosity and better battery performances.

GRAPHICAL ABSTRACT



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ABSTRACT

Polypropylene (PP)/polyethylene (PE) multilayer separators with cellular-like submicron pore structure for lithium-ion battery are efficiently fabricated by the combination of multilayer coextrusion (MC) and thermal induced phase separation (TIPS). The as-prepared separators, referred to as MC-TIPS PP/PE, not only show efficacious thermal shutdown function and wider shutdown temperature window, but also exhibit higher thermal stability than the commercial separator with trilayer construction of PP and PE (Celgard® 2325). The dimensional shrinkage of MC-TIPS PP/PE can be negligible until 160 °C. In addition, compared to the commercial separator, MC-TIPS PP/PE exhibits higher porosity and electrolyte uptake, leading to higher ionic conductivity and better battery performances. The above-mentioned fascinating characteristics with the convenient preparation process make MC-TIPS PP/PE a promising candidate for the application as high performance lithium-ion battery separators.

1. Introduction

Improvements in safety are still urgently required for the wider acceptance of lithium-ion batteries (LIBs) especially in the newly growing application fields such as electric vehicles and aerospace systems [1]. The shutdown function of separators is a useful strategy for the safety protection of LIBs by preventing thermal runaway reactions [2]. Compared to the single layer separators, polypropylene (PP)/polyethylene (PE) bilayer or trilayer separators are expected to provide wider shutdown window by combining the lower melting temperature of PE with high melting temperature and high strength of PP [2,3]. The traditional method to prepare such kind of bilayer or trilayer separators is bonding the pre-stretched microporous monolayer membranes into bilayer or trilayer membranes by calendaring, adhesion or welding, and

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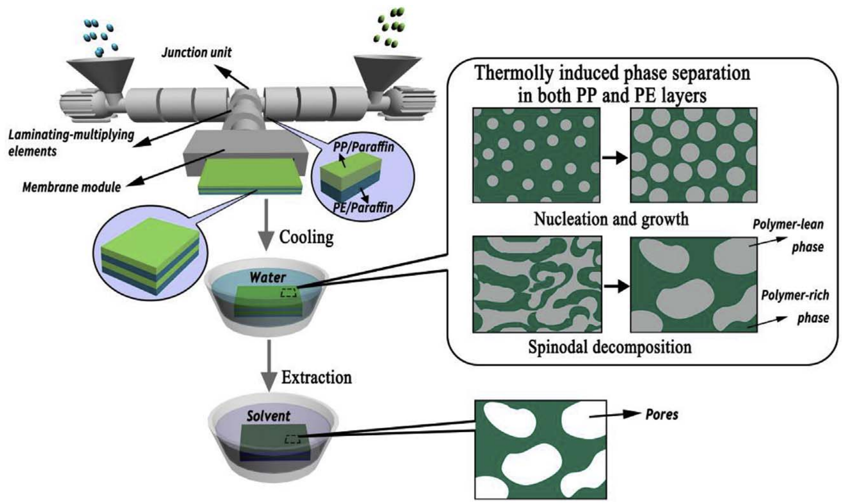

Fig. 1. Schematic illustration showing the preparation process of MC-TIPS PP/PE via the combination of multilayer coextrusion and thermal induced phase separation.

then stretched to obtain the required thickness and porosity [4], which will enhance the mechanical strength but decrease the production efficiency. Moreover, such kind of separators will suffer significant shrinkage at high temperature due to the residual stresses induced during the stretching process, hereby a potential internal shorting of the cell could occur [5]. During the past decades, various modifications have been devoted to improve the dimensional and thermal stability of separators including the surface dip-coating of organic polymers or inorganic oxides [6,7], and chemically surface grafting [8,9]. However, the coated layers are easy to fall off when the separators are bent or scratched during the battery assembly process [10]. Besides, most of the above approaches focused on modifying or reinforcing the existing separators [11], which makes the manufacturing process more complicated and the separators more expensive [1]. Thus it is essential to find new solutions that can optimize the thermal stability, shutdown property, and electrochemical performance without sacrificing the convenient and cost-effective preparation process.

Multilayer coextrusion (MC) represents an advanced polymer processing technique which is capable of economically and continuously producing multilayer materials [5]. Thermal induced phase separation (TIPS) is a widely used manufacturing process for commercial LIBs separators [12], which is based on a rule that a polymer is miscible with a diluent at high temperature, but demixes at low temperature [13]. The separators prepared by TIPS process show well-controlled and uniform pore structure, high porosity, and good modifiability [5]. To the best of our knowledge, no studies have been reported on the combination of the above two methods to prepare multilayer porous separators. Thus in the present study, a novel strategy is proposed to prepare the multilayer LIBs separators comprising alternated layers of microporous PP and PE layers via the combination of multilayer coextrusion and TIPS method, aim to combine the advantages of both methods. Besides, in this work the TIPS composed of a binary system, including one polymer (PP or PE), one diluent (paraffin) and therefore only one extractant (petroleum ether). Hence, the extractant is recyclable and offers higher reproducibility, which is of critical importance for the cost reduction and environmental protection [14]. Another key benefit of this method is that the one-step route provides a more efficient way for large scale fabrication of multilayer separators with high porosity. More significantly, the porous structure is formed without traditional stretching process, which is in favor of the dimensional and thermal stability. The thermal shutdown property and thermal stability of the resultant separators are expected to be improved obviously compared to the commercial bilayer or trilayer separators. The as-prepared separators are also expected to exhibit cellular-like and submicron grade porous structure, sufficient electrolyte uptake, high ionic conductivity, and good battery performance. These advantages make such kind of multilayer membranes a promising alternative to the commercialized bilayer or trilayer LIBs separators at elevated temperatures.

2. Experimental

2.1. Materials

Polypropylene (V30G), polyethylene (Q210), and paraffin wax (66#) were purchased from Sinopec Shanghai Petrochemical Co. Petroleum ether (AR) was purchased from Sinopharm Chem. Reagent Co. The commercialized PP/PE/PP trilayer separator Celgard® 2325 (25 μm microporous PP/PE/PP trilayer membrane) and commercialized PE separator (SK Energy) were provided by Shenzhen Yuanchenghui Electronic Co. Prior to the preparation, PP, PE, and paraffin wax were dried at 50 °C for 24 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

Prior to the multilayer coextrusion, paraffin wax as diluent and PP (or PE) resin with the mass ratio of 55: 45 were mixed and put into the twin-screw extruder to prepare the PP/paraffin and PE/paraffin masterbatches. The schematic illustration of preparation process through the co-joint of MC and TIPS is shown in Fig. 1. The mechanism of the multilayer coextrusion has been reported in our previous work [15]. In this study, the layer number is chosen to be 4. After the multilayer coextrusion, the extruded multilayer membranes were immersed in water immediately at 20 °C to conduct the thermal induced phase separation. The principle of TIPS is that a homogeneous polymer/diluent system would be thermodynamically unstable when rapidly cooling the solution below a bimodal solubility temperature. Firstly the initial phase separated structure were formed through the nucleation and growth process [16,17], then the phase separated droplets come together during the spinodal decomposition [16,17], proceed to minimizing the interfacial free energy [17]. This coarsening process was induced by a differential interfacial tension between the polymer-lean and polymer-rich phases due to the reduction in surface energy associated with the interfacial area [17,18]. The two-phase structures formed by the phase separation were the prototype of pore structures [19]. After the multilayer coextrusion and the thermal induced phase