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# Preparation and performance of polymer electrolyte based on poly(vinylidene fluoride)/polysulfone blend membrane via thermally induced phase separation process for lithium ion battery

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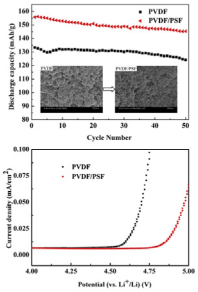
## HIGHLIGHTS

- Polymer electrolyte based on PVDF/PSF blend membrane was prepared via TIPS process.
- Blending PSF promoted the nucleation of PVDF, decreased the size of PVDF spherulite.
- Blending PSF increased the electrochemical stability window of polymer electrolytes.
- Blending PSF markedly enhanced large current charge/discharge performance of cells.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Poly(vinylidene fluoride)/polysulfone (PVDF/PSF) blend microporous matrix of polymer electrolyte for lithium ion battery is prepared via thermally induced phase separation (TIPS) technique. Because of only one parameter, i.e., the PSF/PVDF weight ratio, the membrane microstructure is conveniently controlled. The membrane formation mechanism of PVDF/PSF blend membranes is proposed with the assistance of a binary PSF/PVDF weight ratio-temperature phase diagram. In addition to studying the microstructure and mechanical properties of PVDF/PSF blend membrane, the relationship between properties of membrane, electrochemical performances of corresponding polymer electrolyte and membrane microstructure are also discussed in this paper. It is found that the addition of PSF not only increases ionic conductivity and electrochemical stable window of polymer electrolyte, but also markedly enhances charge–discharge performances of coin cell. The results reveal that PVDF/PSF blend microporous membranes prepared via TIPS technique can be used as polymer matrices of polymer electrolytes for lithium ion batteries.

## 1. Introduction

Lithium ion batteries have been widely applied in portable electronics, electrical vehicles, large power sources and energy storage equipments due to the high specific energy, high efficiency and long cycle life. However, scaling up the lithium battery technology for these applications is still problematic since safety issue

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is still to be solved [1]. The safety issue of a lithium ion battery is mainly caused by the usage of liquid organic solvents in the electrolyte. Alternatively, polymer electrolyte provides an ideal way to solve the safety issue due to its adaptation to various geometries and safety [2]. Generally, two methods are employed to prepare polymer electrolytes. The most common approach is solvent casting [3,4]. According to this method, a mixture of polymer, a lithium salt, and a plasticizer is formed in a glove box and cast to form a gel polymer electrolyte (GPE). However, the mechanical strength of GPEs is poor because they were softened by the addition of liquid electrolyte. Chemical cross-linking based on polyolefin separators is a useful way to enhance mechanical properties and dimensional stability. For example, Q. Lu et al. [5] prepared hydrophilic polytetrafluoroethylene (PTFE)-supported GPE based on the cross-linked poly (ethylene glycol) and poly (glycidyl methacrylate) block copolymer (PEG-b-PGMA). The poly (ethylene glycol) side chains of PEG-b-PGMA can hold the liquid electrolyte inside GPE and PTFE offers mechanical support. The results showed that GPE not only exhibits good electrochemical performances, but also demonstrates non-flammability and good dimensional stability at elevated temperature. The phase inversion technique, suggested by Gozdz and coworkers [6], is another popular method to prepare polymer electrolyte [7,8]. This method involves an activation process in which a membrane is soaked in an electrolyte solution to form polymer electrolyte. Compared with the solvent casting technique, this technique requires critical moisture control only during the assembling process. In the activation process of the phase inversion technique, the liquid electrolyte immerses in the pores and swells the amorphous phase of the membrane. The research of Saito et al. [9] suggests that both pore structure and amorphous domain of microporous membrane influence the ionic conductivity and electrolyte reservation of corresponding polymer electrolyte. Therefore, the performance of polymer electrolyte can be improved by controlling the pore structure and the ratio of amorphous domain of microporous membrane.

In the phase inverse technique, microporous membranes have been extensively prepared by Bellcore's technology or non-solvent induced phase separation (NIPS) technique. Recently, a few studies have been reported on the preparation of microporous membranes via thermally induced phase separation (TIPS) technique. The TIPS process begins by dissolving a polymer in a diluent at a higher temperature. The solution is then cast or extruded into the desired shape (flat sheet, hollow fiber, etc.) and cooled to induce phase separation and polymer solidification (crystallization or glass transition). The diluent is extracted by solvent exchange to yield a microporous structure. When thermal energy is removed, the homogeneous polymer/diluent system can occur via solid–liquid (S–L) or liquid–liquid (L–L) phase separation depending on the polymer–diluent interaction, the composition and the thermal driving force [10]. In comparison to other membrane preparation techniques, TIPS technique is more reliable for controlling the membrane structure because the factors of influencing membrane structure are fewer. Moreover, the membranes prepared via TIPS technique show higher porosity and excellent mechanical strength [11–15].

Semi-crystalline PVDF shows some prominent advantages, such as good electrochemical stability and good affinity with liquid electrolyte. Therefore, PVDF is considered as the next generation polymer matrix candidate for higher performance lithium ion batteries [16,17]. The research of Ji et al. [11] showed that TIPS technique was an effective method to prepare PVDF matrix, and ionic conductivity of corresponding polymer electrolyte was more than $1.0 \times 10^{-3}$ S cm$^{-1}$ at 25 °C. The value reached the standard of practical application for lithium ion batteries [18].

Blending is a simple and effective method to improve the performance of microporous membranes. When a blend is added to a polymer/diluent system, the interaction between polymer and diluent is changed and the crystallization process of crystalline polymer is influenced. That is, blending changes the thermodynamics and kinetic of phase separation process for a polymer/diluent system [11,19–21]. Therefore, the pore structure can be controlled. Several blend membranes, such as poly (vinyl butyral) (PVB)/pluronic F127 (F127) [19], poly(ethylene-co-vinylalcohol) (EVOH)/poly(vinylpyrrolidone) (PVP) [20] and high density polyethylene/poly(ethylene-block-ethylene glycol) (HDPE/PE-b-PEG) [21], had been prepared via TIPS technique and investigated. In recent years, some studies on PVDF blend matrix for polymer electrolyte have been carried out. For example, Cui et al. [22] prepared PVDF/polyethylene oxide-co-polypropylene oxide-co-polyethylene oxide (PEO-PPO-PEO) blend matrix and the ionic conductivity of corresponding polymer electrolyte was more than $1.0 \times 10^{-3}$ S cm$^{-1}$ at 20 °C. Ma et al. [23] prepared PVDF/poly(-methyl methacrylate) (PMMA) blend matrix. It was found that PMMA reduced electrolyte leakage significantly. These investigations indicated that the PVDF blend membrane prepared via TIPS technique can be used as the polymer microporous matrix of polymer electrolyte for lithium ion batteries.

Nevertheless, there still exist some problems for the two systems in Refs [22,23]. For example, during the cooling process, the PVDF/PEO-PPO-PEO/diluent system underwent S–L phase separation and large spherulite structure was formed. The addition of PEO-PPO-PEO could not decrease spherulite size. It is clear that larger spherulite size decreases the mechanical properties of membrane and leads to the wider pore size distribution. Moreover, the electrochemical stability window of the two polymer electrolytes decreases with the addition of blend polymer. To overcome these disadvantages, PSF is selected to blend with PVDF in this study. On one hand, PSF is only partially compatible with PVDF [24–26]. Therefore the addition of PSF can weaken the interaction between PVDF and diluent. i.e., PSF can influence the membrane formation mechanism and control membrane structure. On the other, the rigid segments of benzene ring in PSF molecules have the ability to promote the nucleation for PVDF crystallization and thus decrease the spherulite size of PVDF. Finally, PSF is a kind of amorphous polymer and has a good affinity with liquid electrolyte. This suggests that blending PSF may increase the performance of the polymer electrolytes.

In this study, firstly, PVDF/PSF blend membranes were prepared by TIPS technique. Then, the membranes were soaked in liquid electrolyte and activated to form polymer electrolytes. The aim of the present study was to demonstrate the effect of PSF on the membrane formation mechanism of PVDF/diluent system and control the membrane structure systematically by varying PSF/PVDF weight ratio. The relationship between performances of membrane, electrochemical properties of corresponding polymer electrolyte and final membrane microstructure were also discussed in this paper.

## 2. Experimental

### 2.1. Materials

PVDF (Solef 1015, Mn = $3.37 \times 10^5$, Mw = $5.73 \times 10^5$) was purchased from Solvay Silexis, Belgium. PSF ($\eta = 0.62$) was purchased from Dalian polysulfone Plastic Co. Ltd., P. R. China. PVDF and PSF were dried in a vacuum oven at 50 °C for 48 h before use. The mixture, composed of diethylene glycol dibenzoate (DEDB, provided by Shanghai Chemical Reagent Co., Ltd.) and dibutyl phthalate (DBP, provided by Tianjin Guangfu Fine Chemical