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# Preparation and Properties of Poly (vinylidene fluoride)/poly(dimethylsiloxane) *graft* (poly(propylene oxide)-*block*-poly(ethylene oxide)) blend porous separators and corresponding electrolytes

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ABSTRACT

This work aims exploring the high performance porous separators that can be activated into gel electrolyte membranes for lithium ion batteries. A comb-like copolymer poly (dimethylsiloxane) graft poly (propylene oxide)-block-poly (ethylene oxide) (PDMS-g-(PPO-PEO)) was synthesized and blended with poly (vinylidene fluoride) (PVDF) to fabricate porous separators via a typical phase inversion process, and then the separators absorbed liquid electrolyte solution and formed into polymer electrolyte membranes. By measuring the composition, morphology and ion conductivity etc, the influence of PDMS-g-(PPO-PEO) on structure and properties of blend separators were discussed. Compared with pure PVDF separator with comparable porous structure, the adoption of PDMS-g-(PPO-PEO) decreased the crystallinity and increased the liquid electrolyte uptake and stability effectively. It was also found that the electrode/electrolyte interfacial resistance could be reduced greatly. The resulting electrolyte membrane using separator with PVDF/PDMS-g-(PPO-PEO) mass ratio in 8/2 exhibited highest ionic conductivity in $4.5 \times 10^{-3}$ S/cm at room temperature, while the electrochemical stability was up to 4.7 V (vs. Li/Li$^+$). Coin cells assembled with such separators also exhibited stable cycle performance and improved rate capabilities, especially when discharge rate higher than 0.5 C.

## 1. Introduction

Lithium ion batteries (LIBs) using liquid electrolytes may cause various safety hazards, such as fire, burn and explosion [1]. An available method to solve the safety and reliability problem is to use gelled polymer electrolytes (GPEs) as the substitute of the liquid electrolytes due to its much lower vapor pressure and combustibility [2–5]. Among the GPEs reported so far, microporous polymer electrolytes have been in the spotlight because of their high room temperature conductivity (>$10^{-3}$ S cm$^{-1}$) which is sufficient for practical applications in lithium ion batteries [6–8]. Polymers such as polyvinylidene fluoride (PVDF) [9], polyacrylonitrile (PAN) [10], poly(methyl methacrylate) (PMMA) [11], and poly(ethylene oxide) (PEO) [12] have been studied in microporous polymer electrolytes. PVDF draw a great attention on account of its excellent properties, such as mechanical strength, high chemical resistance, good thermal stability, higher dielectric constant ($\varepsilon \approx 8.3$) and strongly electro-withdrawing functional groups (-C-F) [13]. However, the limitations of porous PVDF membranes for separator applications include poor stability of entrapped liquid electrolyte, high crystallinity of polymer matrix and corresponding low ion conductivity [4].

To our knowledge, there are several effective strategies that have been adopted to improve the affinity between separators and liquid electrolyte, which can be classified to surface grafting [14], surface coating [15] and blending with amphiphilic polymers [16]. Among these strategies, surface modifications may substantially block the membrane pores and result in a reduced liquid electrolyte uptake. In comparison, membrane modification by blending with an amphiphilic copolymer is more convenient and practical for large-scale production, because it doesn't need further treatment after the fabrication of membranes and has well-control on membrane structure. And on the other hand, the appropriate hydrophobic part of the amphiphilic copolymer would effectively decrease the crystallinity of the polymer matrix, which is beneficial for liquid electrolyte uptake. Polymers contain PPO or PEO chains had been proved to have a positive effect on decreasing crystallinity and increasing uptake of liquid electrolyte. Cui et al. [17] reported a kind of PVDF/PEO-PPO-PEO blend microporous membrane via thermal induced phase separation(TIPS) for

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lithium ion batteries. Results showed the adoption of PEO-PPO-PEO dramatically increased both uptake of blend membranes and ionic conductivity of corresponding polymer electrolytes. Yu et al. [18] synthesized PVDF-HFP-g-PPEGMA copolymer through atom transfer radical polymerization (ATRP) method and prepared corresponding gel electrolytes. Due to the strong affinity of PEGMA chains with liquid electrolyte, the electrolyte uptake and ion conductivity are dramatically improved with respect to the PVDF-HFP separators.

Polysiloxane has been widely used as gel electrolyte material due to its several advantages, including low surface tension, low glass transition temperature, high temperature stability, chemical inactivity, unique flexibility and so on [19]. Polysiloxane based comb-like polymer or copolymer electrolytes had high ionic conductivity because of its flexibility. Shibata et al. [20] prepared poly(ether urethane) (PEU)/polysiloxane/$LiClO_4$ blending electrolytes for lithium battery. They found the adoption of polysiloxane could increase both the ion mobility and ion density, which resulted in the improvement of conductivity.

In our previous works [21], poly (dimethylsiloxane)(PDMS) was used as modified agent to prepare porous PVDF separators for lithium ion cells. It has been found the adoption of PDMS not only decreases the crystallinity and increases the breaking elongation efficiently, but also enhances the stability of entrapped liquid electrolyte and ion conductivity. In this work, an amphiphilic poly (dimethylsiloxane) graft poly (propylene oxide)-block-poly (ethylene oxide) (PDMS-g-(PPO-PEO)) was designed and synthesized and a series of blend separators were prepared via the phase inversion method. The morphology of separators and effect of PDMS-g-(PPO-PEO) on crystallinity and electrode/electrolyte interfacial stability were studied. Finally, electrochemical properties of corresponding polymer electrolytes were studied.

## 2. Experimental

### 2.1. Materials

PVDF (HSV 900, $M_w = 1.8 \times 10^6$,) was kindly supplied by Arkema Ltd and used as received. Hydrogen polysiloxane and poly (propylene oxide- ethylene oxide) was purchased from Sinopharm Chemical Reagent Company. Platonic-chloride was procured from Green Chemical Company, China. The solvent of *N*,*N*-dimethylacetamide (DMAc), toluene and DMSO were obtained from Shanghai Chemical Company. Liquid electrolyte solution ($LiPF_6$ concentration 1 mol/L, EC/DMC/EMC = 1/1/1 by weight) was supplied by Guotai Huarong Company, China. The cathode $LiFePO_4$ and anode carbon were kindly provided by Wanxiang Company, China.

### 2.2. Synthesis of PDMS-g-(PPO-PEO)

Details of the synthesis process of PDMS-g-(PPO-PEO) had been reported in our previous work [22]. It can be summarized as follows. Toluene was employed as solvent and platonic-chloride as catalyzer in the synthesis process. Poly(dimethylsiloxane) graft poly(propylene oxide)-block-poly(ethylene oxide)(PDMS-g-(PPO-PEO)) was obtained through hydrosilylation reaction of hydrogen polysiloxane and unsaturated glycidyl ether, poly(propylene oxide-ethylene oxide) for 4-5 h under the $N_2$ protection at about 85 °C. Gel permeation chromatography (GPC) analysis (Waters 1515, USA) of PDMS-g-(PPO-PEO) was conducted at 30 °C in DMF containing 0.5% lithium bromide with a flow rate of 1 ml/min, using narrow dispersed PMMA as calibration standard. Result of the GPC test showed that $M_n$ of PDMS-g-(PPO-PEO) was $2.5 \times 10^4$ (PDI = 1.44), the contents of PPO and PEO chain were 38.7 *wt%* and 44.0 *wt%* respectively.

### 2.3. Preparation of porous PVDF/PDMS-g-PPO-b-PEO separators

PVDF and PDMS-g-(PPO-PEO) were dissolved in DMAc at 70 °C under stirring over 8 hours to yield a homogenous solution. After completely release of bubbles, the solution was cast onto glass plate and immersed into a mixed coagulation bath constituted with DMAc/water (6/4) bath of 30 °C. The formed porous membranes were taken out and washed with de-ionized water for 24 h. At last the blend membranes (e.g., separators) were dried in vacuum at 40 °C prior to structure and property measurements.

### 2.4. Characterization of PVDF/PDMS-g-(PPO-PEO) separators

The chemical structure of blend separators were characterized by $^1$H-NMR measurement (300 MHZ, Bruker) using DMSO as solvent. The morphology of separators was imaged on a field-emission scanning electron microscope (SEM, SIRION-100, Ltd). The porosity and pore size were measured using a mercury porosimeter (Auto Pore IV 9500, USA) with sample weight of about 100 mg. The crystalline was investigated through X-ray diffraction (X'Pert PRO, PANalytical B.V., Netherlands) with CuKa radiation and DSC measurement (TA-DSC, PerkinElmer, USA). The mechanical properties were tested by an electro-tensile testing machine (RGM-4000, Shenzhen, China) using a sample of size 80 × 10 mm. X-ray photoelectron spectroscopy (XPS, PHI-5000 C, Perkin-Elmer) was used to analyze the surface chemical compositions of the separators with the takeoff angle of 60°, which correspond to the sampling depths of 3.15nm[23]. Surface energy was characterized on the basis of a contact angle system (OCA20, Dataphysics, Germany) equipped with video capture at room temperature (25 °C).

### 2.5. Electrochemical performance of PVDF/PDMS-g-(PPO-PEO) separators

In the electrolyte solution uptake measurement, the weighted separator piece of size 20 × 20 mm was immersed in electrolyte solution at 25 °C till soaking saturation (over 24 hours). The electrolyte solution uptake ($\Delta W$, *w%*) was determined by the following equation $\Delta W = ((W_s - W_0)/W_0)$*100%, where $W_s$ and $W_0$ were the weights of the wet and dry separator, respectively. The stability of trapped electrolyte was monitored from the weight change of the wet separator which was placed in a value bag under dry argon atmosphere at 25 °C.

The ionic conductivities ($\delta$) of polymer electrolytes were measured by the AC impedance method as described before [21]. The sample was sandwiched between two stainless steel electrodes and then the assembly was submitted to bulk resistance ($R_b$) measurement (in frequency range of 1-1 × $10^6$Hz at amplitude of 5 mV) on an electrochemical work station system (CHI 660 C, China) at 25 °C. The $\delta$ value was calculated following $\delta = d/(R_b \cdot A)$, where $d$ and $A$ were the thickness and area of the separator respectively. The same conditions were applied at room temperature on Li/electrolyte/Li cells for the investigations of electrode/electrolyte interfacial characters.

The electrochemical windows of polymer electrolytes were studied by the linear sweep voltammetry method performed on a working electrode of stainless steel and a counter and reference electrode of lithium-metal at a scan rate of 1.0 mV $s^{-1}$. A unit cell (2025-type coin) was assembled by sandwiching a separator between a $LiFePO_4$ cathode and a natural graphite