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Gel polymer electrolytes based on active PVDF separator for lithium ion battery. I: Preparation and property of PVDF/poly(dimethylsiloxane) blending membrane

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ABSTRACT

This work explores the “active” separator that can be activated into gel or polymer electrolyte membrane. The active nature and easier processing property make the separator more applicable in assembling batteries. To improve the activeness of PVDF based separators, the poly(dimethylsiloxane) (PDMS) was blended into porous PVDF membrane matrix via a typical phase inversion route. By measuring the composition, morphology, ion conductivity, and so on, the work studies the influence of PDMS on structure and properties of blending separators. Compared with pure PVDF membrane having comparable porous structure, 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. For separators with PVDF/PDMS mass ratio in 7/3, the liquid electrolyte uptake reached 250 wt% and ion conductivity of formed gel electrolyte membrane was 1.17×10^{-3} S cm^{-1}, which was acceptable for high voltage lithium ion batteries.

1. Introduction

The remarkable development of portable electronic devices has led to increasing demand on lithium ion battery (LIB) with high energy densities and capacities to facilitate compact and lighter portable electronic equipment [1–4]. By replacing the liquid electrolyte currently in use, the gel polymer electrolyte yields several advantages including high energy density, structural stability, and low volatility. A lot of polymers, such as polyethylene oxide (PEO) [5], polyacrylonitrile (PAN) [6], polymethylmethacrylate (PMMA) [7], poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride-co-hexafuoropropylene) (PVDF-HFP) [8], have been used as matrices for polymer electrolytes. Due to its appealing properties such as high dielectric constant ($\varepsilon \approx 8.4$) and strongly electron withdrawing functional groups (–C–F–), PVDF based fluorine polymer is considered as the next generation separator candidate for high performance lithium ion batteries [9,10]. However, the limits of porous PVDF membrane for separator application lie in the poor stability of entrapped liquid electrolyte, the higher crystallinity of PVDF, and corresponding low ion conductivity. To the best of our knowledge, two methods are usually used to decrease the crystallinity of the polymer matrix. The first method is by incorporating asymmetric groups to the main chains of the polymer. The other method, which is more widely adopted, is by blending the polymer matrix with suitable polymers. Xiao et al. [11] synthesized PEO-b-PMMA copolymer through the atom transfer radical polymerization (ATRP) method and prepared PVDF/PEO-b-PMMA blending separators. PMMA segments had excellent compatibility with PVDF, and PEO segments improved the porous structure of the polymer membrane to enhance the electrolyte uptake. Zhao et al. [12] reported an amphiphilic hyperbranched-star polymer (HPE-g-MPEG) and blended it with PVDF to fabricate a porous membrane via typical immersion precipitation process. It was found that the introduction of HPE-g-MPEG resulted in significant increase in porosity and remarkable reduction in crystallinity, which consequently led to a substantial increase in ion conductivity at ambient temperature. Given the complex property of ATRP method and such synthesized process, if there existed one convenient polymer having one or two characteristics of the copolymers, it would also be used as an additive to prepare separators based on PVDF matrix.

Polysiloxane is one of the most commonly used rubbery membrane materials characterized by several advantages, including low surface tension, unique flexibility, low glass transition temperature, high temperature stability, chemical inactivity, insulating stability, shear stability, high compressibility and so on [13]. Sadrzadeh et al. [14] casted poly(dimethylsiloxane) (PDMS) solution on PES support material to prepare composite separation membrane. The prepared macroporous PES membrane was impregnated by distilled water, and PDMS casting solution of specified concentration was poured on it. After solvent evaporation, the composite PDMS/PES mem-

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brane was prepared. Zhen et al. [15] prepared composite membrane with lower surface tension for separation of volatile organic compounds (VOCs) by coating a very thin PDMS layer onto PVDF hollow-fiber substrate via a developed dip coating method. When polysiloxane was introduced into the main chain of the comb-like polymers or copolymers, the obtained polymer electrolytes had high ionic conductivity because of the flexibility of the polysiloxane segment [16]. Shibata et al. [17] studied the electrochemical properties of poly(ether urethane) (PEU)/polysiloxane and $LiClO_4$ blending dense membrane used as electrolyte in lithium ion battery. Polysiloxane was found to be beneficial to the increase of both the ion mobility and ion density, which resulted in the improvement of the conductivity.

To our best knowledge, few studies on the blending of polysiloxane with the PVDF polymer materials have been reported. Can polysiloxane be used to modify this polymer matrix via a typical liquid type battery making route? If yes, such modified PVDF membrane should be named as “active separator”, which can be activated to gel electrolyte by absorbing lithium salt liquid electrolyte inside the assembled battery after layered stacks of cathode/separator/anode have been loaded into the shell. In this work, porous PVDF/PDMS active separators for LIBs were proposed and prepared following a phase inversion route. Based on structural and electrochemical measurements, the influences of PDMS on porous PVDF separators were investigated.

2. Experimental

2.1. Materials

PVDF ($M_w = 1.8 \times 10^6$, HSV 900) was kindly supplied by Arkema Ltd and used as received. PDMS ($M_w = 5 \times 10^4$) was purchased from Dow Corning Company. The solvent of *N*,*N*-dimethylacetamide (DMAc), DMSO-d_6 and pore size controlling reagent of glycerol were obtained from Shanghai Chemical Company. The electrolyte solution of $LiPF_6$ in mixture solvent of ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) ($LiPF_6$ concentration, 1 mol/L, EC/DMC/EMC = 1/1/1 by weight) was supplied by Guotai Huarong Company, China.

2.2. Preparation of porous PVDF/PDMS separators

PVDF, PDMS and co-solvent of glycerol were dissolved in DMAc at 70 °C under stirring over 8 h to yield a homogenous cast solution. In an air atmosphere with relative humidity of 60–70% and temperature of 24–26 °C, the solution was cast into 150 μm thick liquid film on glass plate. After evaporating for 10 s, the supported liquid film was immersed into water bath with temperature of 30 °C and the solidified porous blending membrane formed. Washing the membrane in water of 30 °C over 48 h was adopted to remove glycerol, solvent and additives. After being dried in vacuum at 40 °C over 24 h, the blending PVDF/PDMS membrane (e.g., porous separator) was obtained for structure and property measurements.

2.3. Characterization of PVDF/PDMS separators

The chemical compositions of prepared separators were characterized via ^1H NMR measurement (300 MHz, Bruker) by dissolving the separator in DMSO-d_6. The morphology of separator was imaged on field-emission canning electron microscopy (FE-SEM, Hitachi S-4700, Japan). The porosity was measured on a Pore Size analyzer (Auto Pore IV 9500, Micromeritics, USA). The crystalline was investigated from the wide-angle X-ray diffraction (WAXD) patterns taken on a X-ray diffractometer (X'Pert PRO, PANalytical B.V., Netherlands) with Cu Kα radiation and differential scanning calorimetry (DSC) (TA-DSC, PerkinElmer, USA). The mechanical properties were tested by AG-1 electro-tensile testing machine (Shimadzu, Japan) using the sample in size of 80 mm × 10 mm.

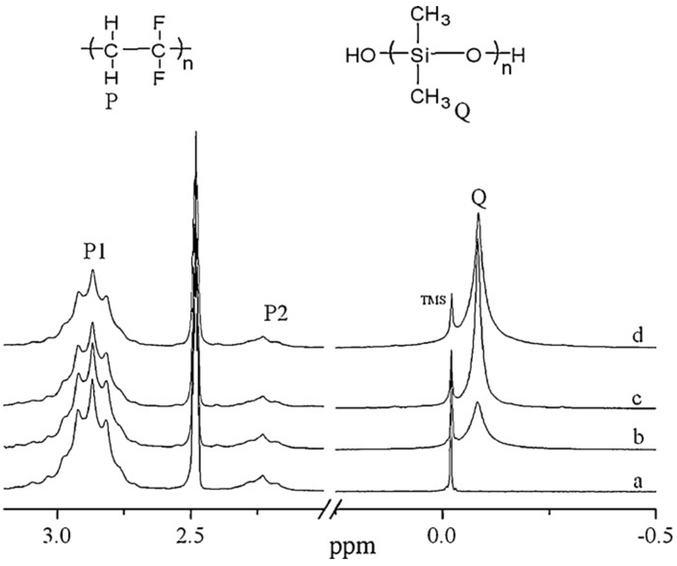

Fig. 1. ^1H NMR spectra of porous separators with different PVDF/PDMS ratio in casting solutions: (a) 10/0; (b) 9/1; (c) 8/2; (d) 7/3.

2.4. Electrolyte solution uptake and ion conductivity of separators

In electrolyte solution uptake (ΔW, wt%) measurement, the weighted separator piece with size of 30 mm × 30 mm was immersed in electrolyte solution at 25 °C till the soaking saturation (over 24 h). After being taken out and the excessive electrolyte solution at the surface slightly absorbed using tissue, the soaked separator was weighted and the electrolyte solution uptake was calculated using equation $\Delta W = ((W_s - W_0)/W_0)^*100\%$, where, W_s and W_0 were the weight of soaked and dried separator, respectively. The uptake stability was monitored from weight change of the soaked separator in a dry argon atmosphere at 25 °C. During ionic conductivity (δ) measurement, the soaked separator disk (in diameter of 10 mm) was sandwiched between two stainless steel blocking electrodes (the assembly was sealed in a Teflon cell), and then the assembly was submitted to bulk resistance (R_b) measurement in frequency range of 1 to 10^5 Hz at amplitude of 5 mV on an electrochemical work station system (Princeton Applied Research 2273, PARC, USA) at 25 °C. The ionic conductivity was calculated following $\delta = d/(R_b A)$, where, d and A were the thickness and area of the separator disk, respectively. Using the same soaked separator sandwiched between a lithium metal counter electrode and a stainless steel working electrode (the assembly was also sealed in a Teflon cell), a scanning voltage ($1\,mV\,s^{-1}$) was applied starting from the open circuit voltage on the same instrument for electrochemical stability measurement. The decomposition voltage was indicated from the quick current increase point on recorded specific *V*–*I* curve.

3. Results and discussion

3.1. Composition of PVDF/PDMS separators

The pure PVDF and PVDF/PDMS blending separators were prepared through phase inversion process. One important consideration in such preparation route is the reservation of designed composition. To reveal the reservation of PDMS, the ^1H NMR spectra of blending separators dissolved in DMSO-d_6 were obtained as shown in Fig. 1. The proton peak in methyl group of PDMS