Applied Surface Science 440 (2018) 186-192

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc



Preparation and characterization of PVDF separators for lithium ion cells using hydroxyl-terminated polybutadiene grafted methoxyl polyethylene glycol (HTPB-g-MPEG) as additive



Applied Surface Science

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ARTICLE INFO

Article history: Received 2 September 2017 Revised 5 December 2017 Accepted 18 January 2018

Keywords: Poly(vinylidene fluoride) Hydroxyl-terminated polybutadiene Microporous separator Gel electrolyte Lithium batterv

ABSTRACT

Hydroxyl-terminated polybutadiene grafted methoxyl polyethylene glycol (HTPB-g-MPEG) with different arm length were synthesized by grafting methoxyl poly(ethylene glycol)s (MPEGs, M_n = 350, 750, 1900 and 5000, respectively) to the hydroxyl-terminated polybutadiene (HTPB) molecule using isophorone diisocyanate (IPDI) as the coupling agent, and blended with PVDF to fabricate porous separators via phase inversion process. By measuring the composition, morphology and ion conductivity etc., the influence of HTPB-g-MPEG on structure and property of blend separators were discussed. Compared with pure PVDF separator with comparable porous structure, the adoption of HTPB-g-MPEG could not only decrease the crystallinity, but also enhance the stability of entrapped liquid electrolyte and corresponding ion conductivity. The cells assembled with such separators showed good initial discharge capacity and cyclic stability.

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1. Introduction

Microporous polymer membranes are commonly studied for lithium ion cells due to their large pore size and high room temperature conductivity (> 10^{-3} S cm⁻¹). Polymers such as PVDF [1], PAN [2], PMMA [3], and poly(ethylene oxide) (PEO) [4] have been used to prepare microporous membrane through phase inversion method. PVDF draw a great attention on account of its excellent appealing properties, such as mechanical strength, high chemical resistance, good thermal stability, higher dielectric constant and strongly electro-withdrawing functional groups (-C-F) [5]. However, the high crystallinity of PVDF is one of the major causes for the relatively high internal resistance in the lithium ion cells [6]. Nunes-Pereira [7] points out that polymer blends may be one of the most promising ways to improve PVDF based separators. Appropriate polymers can provide improvements on the ionic conductivity, electrochemical stability and cycle performance of battery separators.

A variety of polymers have been adopted to blend with PVDF or its copolymers to prepare microporous membranes, such as PMMA [8], HDPE [9] and so on. Costa [10] improved the solvation problems of PVDF-TrFE separators by using PEO polymers as blend,

* Corresponding author. *E-mail address:* chaochunying@zju.edu.cn (C.-Y. Chao). because PEO has high swelling capability in alkyl carbonatebased electrolyte solutions. It was verified that the pore structure, hydrophilicity and electrolyte uptake of the blend separators strongly depend on the PEO content. In the succeeding work, the authors [11] investigated the physicochemical properties of PVDF-TrFE/PEO (1/1 weight ratio) electrolyte membranes both in organic and ionic liquid solutions and compared that with pure PVDF-HFP and PVDF-TrFE membranes. Although the liquid electrolyte uptake and ion conductivity of PVDF-TrFE/PEO membranes were both lower than the other two polymer membranes, the swollen electrolyte stability was enhanced obviously due to stronger interactions of the solution components with PEO. Different from homopolymers, amphiphilic polymers usually have both hydrophobic and hydrophilic part in one chain structure. When the appropriate amphiphilic polymers were blend with PVDF to prepare membranes through phase inversion method, the hydrophobic part would effectively decrease the crystallinity of the polymer matrix to form amorphous region, which is beneficial for liquid electrolyte uptake. And the hydrophilic part will enrich on the membranes' surface to increase the affinity between the porous matrix and the electrolyte solution and reduce the electrolyte leakage. Zhang [12] reported the PVDF/p(hexafluorobutyl methacrylate-co-poly(ethyleneglycol) methacrylate) (P(HFBMAco-PEGMA)) blend gel polymer electrolyte for lithium ion batteries. When the ratio of P(HFBMA-co-PEGMA) and PVDF was 1.7/10, the



liquid electrolyte uptake and ionic conductivity of the blend separators were up to 387% and 3.19 mS cm⁻¹, respectively. Cui [13] prepared a serious of PVDF/PEO-PPO-PEO blend membranes through thermal induced phase separation (TIPS) for lithium ion batteries. Results showed the adoption of PEO-PPO-PEO could dramatically increase both uptake of blend membranes and ionic conductivity of corresponding polymer electrolytes. Xiao [14] synthesized PEO-b-PMMA copolymer and bended it with PVDF to prepare separators. The PMMA segments had excellent compatibility with PVDF and polyether segments improve the pore structure of the microporous membrane to enhance the electrolyte uptake.

In this work, a series of amphiphilic polymer HTPB-g-MPEG with different arm length were designed and synthesized and corresponding microporous blend separators were prepared via phase inversion method. The morphology of separators and effect of HTPB-g-MPEG fraction on crystallinity and uptake of liquid electrolyte were studied. Finally, electrochemical properties of lithium ion cells using such separators were investigated.

2. Experimental

2.1. Materials

Hydroxyl-terminated polybutadiene (HTPB, $M_n = 5100$, Hydroxyl value = 1.18 mmol g⁻¹) was kindly provided by Qilong Chemical Company, China and used as obtained. Methoxyl poly (ethylene glycol)s (MPEGs, $M_n = 350$, 750, 1900 and 5000), isophorone diisocyanate (IPDI) and dibutyltin dilaurate were bought from Aldrich and used without purification. PVDF ($M_w = 1.8 \times 10^6$, HSV 900) was kindly supplied by Arkema Ltd and used as received. Tetrahydrofuran (THF, Shanghai Chemical Company) was purified by refluxing with calcium hydride (CaH₂, Shanghai Chemical Company) and distilling from CaH₂ to remove water and other impurities. The solvent of *N*,*N*-dimethylacetamide (DMAc), toluene and DMSO-*d*₆ were obtained from Shanghai Chemical Company. The electrolyte solution (LiPF₆ concentration, 1 mol/L, EC/DMC/EMC = 1/1/1 by weight) was supplied by Guotai



(HTPB-g-MPEG)

Fig. 1. Synthesis procedure of copolymer HTPB-g-MPEG.

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