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Polymer electrolytes based on poly(vinylidene fluoride-*co*-hexafluoropropylene) with crosslinked poly(ethylene glycol) for lithium batteries

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ABSTRACT

The combination of a poly(ethylene glycol) (PEG) network and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) copolymer chains is one of the most efficient means for modifying PVDF-HFP gel electrolytes. Previous preparations tend to introduce contamination into the polymer gel electrolyte because of irradiation, high temperature or the initiator needed for crosslinking which might result in the electrochemical degradation. In order to overcome the above disadvantages, a new method has been developed to successfully prepare the semi-interpenetrating polymer networks of PVDF-HFP based electrolytes with crosslinked diepoxy polyethylene glycol (DIEPEG). In this process, impurities are avoided because of a moderate reaction temperature at 50 °C and poly(ethylenimine) (PEI) as the crosslinking agent. Microporous films with various compositions are prepared and characterized. Thermal, mechanical, swelling and electrochemical properties, as well as microstructures of the prepared polymer electrolytes have been investigated using thermogravimetric analysis, electrochemical impedance spectroscopy, linear sweep voltammetry, and scanning electron microscopy. The results show that the blend polymer electrolyte with PVDF-HFP/PEI + DIEPEG (60:40 w/w) has an ionic conductivity of 2.3 mS cm^{-1} at room temperature in the presence of 1 M $LiPF_6$ in EC and DMC (1:1 w/w). All the blend electrolytes are electrochemically stable up to 4.8 V versus Li/Li^+. The results reveal that this new method may be very promising for improving PVDF-HFP based electrolytes.

1. Introduction

In lithium batteries, polymer gel electrolytes are prepared with various matrix polymers such as polyacrylonitrile (PAN) [1], poly (methyl methacrylate) (PMMA) [2], poly(vinyl chloride) (PVC) [3], poly(vinyl pyrrolidone) (PVP) [4], poly(ethylene oxide) (PEO) [5] and poly(vinylidene fluoride) (PVDF) or poly[(vinylidene fluoride)-*co*-hexafluoropropylene] (PVDF-HFP) [6]. Among them, poly[(vinylidene fluoride)-*co*-hexafluoropropylene] is widely used because of the excellent mechanical and chemical stability [7,8]. However, PVDF-HFP films may dissolve in EC-based solvents as a result of heat generated under abusive cell operation and it may also lose carbonate solvent by evaporation upon long storage [9,10]. Various modifying approaches have been proposed in the literature [11–14]. Among them, the semi-interpenetrating polymer networks (SIPN) of PVDF-HFP based electrolytes with crosslinked poly(ethylene glycol) (PEG) have been proved to be one of the most efficient methods [15,16].

Chemical and radiation processes can be adopted to crosslink PEG. PEG was crosslinked by γ-irradiation [17,18] or by UV irradiation in the presence of benzophenone as a photoinitiator [19–21]. Chemical crosslinking of PEG was also reported with reagents such as multi-isocyanate and PEG [15], poly(ethylene glycol) diacrylate (PEGDA) and 2,2′-azobisisobutyronitrile (AIBN) [22], poly(ethylene glycol) (PEG) and tetraethyl orthosilicate (TEOS) [23]. However, all these methods have partial disadvantages. Firstly, the polymer gel electrolyte contains the residual initiator [24]. Secondly, impurities may be brought as by-product arising from irradiation [17,18]. Lastly, high reaction temperature, commonly exceeding 100 °C, tends to produce impurities during chemical crosslink [15]. All these disadvantages might retard the electrochemical performance of lithium battery. To overcome these disadvantages, we have attempted to prepare semi-interpenetrating polymer networks (SIPN) of PVDF-HFP based electrolytes with crosslinked PEG which is formed by PEG400 with both epoxy chain ends (DIEPEG) as a crosslinking oligomer and poly(ethylenimine) (PEI; Mn = 423) as crosslinking agent. During the crosslinking process, no initiator with possible side-effects is applied and the reaction temperature is moderate at 50 °C to avoid the residual impurities.

2. Experimental

2.1. Materials

PVDF-HFP (Kynar Flex LBG-1, Elf Atochem) was dried at 60 °C under vacuum for 16 h before use. Poly(ethylene glycol) (PEG400;

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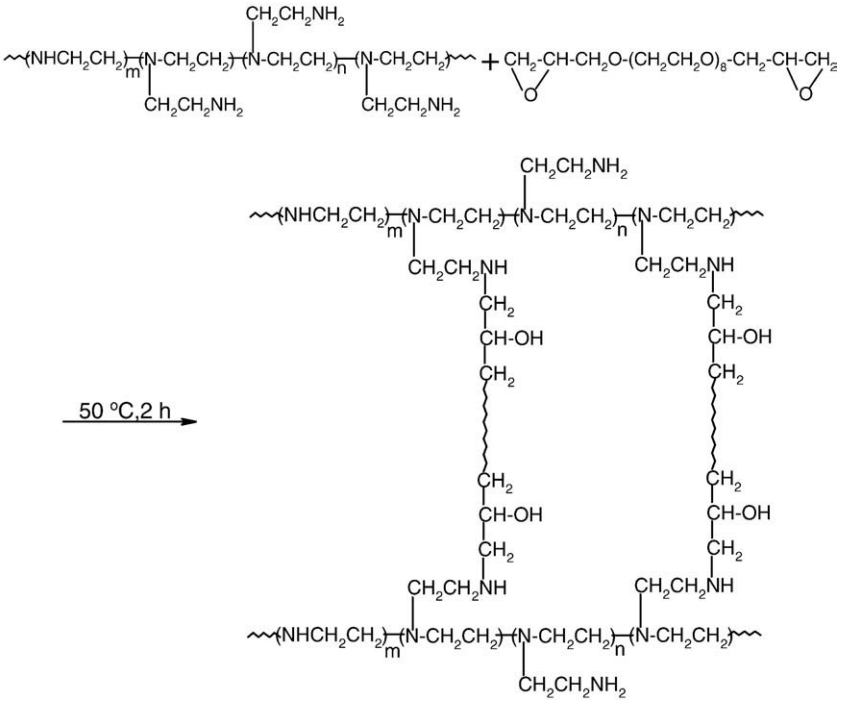

Fig. 1. The crosslinking process for the reaction of PEI with DIEPEG.

Mn = 400; Aldrich) was dehydrated under reduced pressure at 80 °C for 5 h before use. Branched poly(ethylenimine) (PEI; Mn = 423; mol ratio of primary amine/secondary amine/tertiary amine = 1:2:1; Aldrich) was used as received. All the other reagents and chemicals were used without further purification.

2.2. Preparation of polymer electrolytes

PEG with both epoxy chain ends (DIEPEG) was prepared and purified from PEG400 according to literature [25]. The proper PVDF-HFP and PEI were added into a mixture of acetone and deionized water (8:1 w/w) and stirred continuously for 1 h. DIEPEG was then added and mixed for 30 min to form a homogeneous solution. The obtained viscous solution was then cast onto a glass plate using a scalpel. The wet membrane was placed in a ventilating cabinet for 30 min to evaporate the acetone which induced phase inversion. The resulting membrane was immediately put into the oven to crosslink PEI with DIEPEG for 2 h at 50 °C. Afterwards the membrane was dried to evaporate the residual impregnant at 50 °C under vacuum for 24 h. Finally, the semi-interpenetrating polymer networks (SIPN) of PVDF-HFP with crosslinked PEG were obtained. During the preparation, the molar ratio of the amine group in PEI with epoxy group in DIEPEG was optimized to maintain 2:1 all the time. The weight proportion of PVDF-HFP + DIEPEG + PEI with deionized water was maintained at 1:1. In this formulation, various ratios of PVDF-HFP/DIEPEG + PEI were prepared and tested.

The dry microporous membranes were activated by soaking them for 3 h in an electrolyte solution composed of 1 M $LiPF_6$ in EC and DMC (1:1 w/w). After swelling, the excess liquid electrolyte on the surface was removed by pressing lightly between two sheets of filter paper. The activation process above was completed in the glove box (MBRAUN MB 150B-G-11, Germany) filled with dry argon.

2.3. Characterization and electrochemical measurements

In order to investigate the extent of crosslinking of polymer networks, an attenuated total reflection Fourier transform infrared spectrometer (ATR-FTIR, Nicolet AvaTar 360) was used over the range of wavenumber of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} and 64 scans,

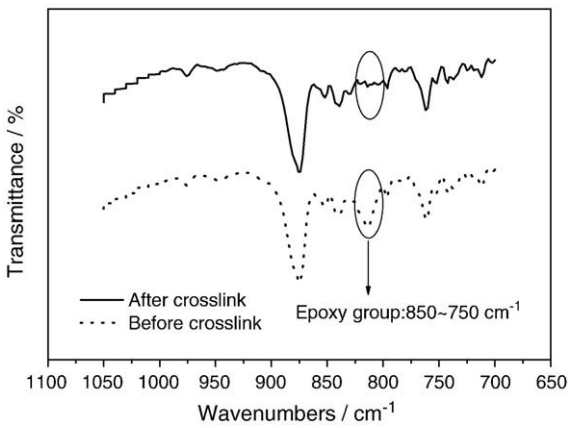

Fig. 2. ATR FT-IR spectra of PVDF-HFP/PEI + DIEPEG polymer membrane before and after crosslinking reaction (PVDF-HFP/PEI + DIEPEG = 60:40 w/w).

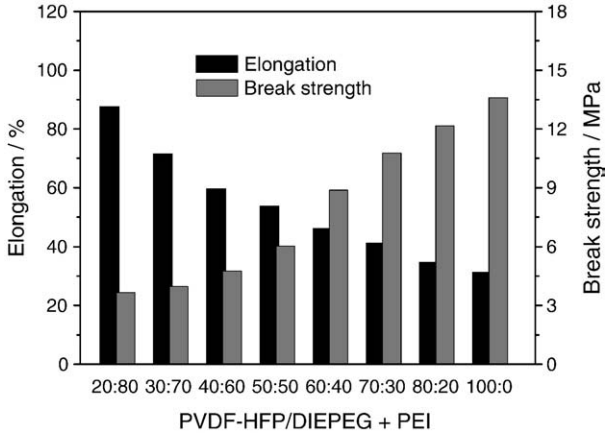

Fig. 3. Maximum tensile strength and break elongation curves with different compositions of PVDF-HFP/PEI + DIEPEG blend membranes.