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Pre-irradiation grafted single lithium-ion conducting polymer electrolyte based on poly(vinylidene fluoride)

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ABSTRACT

In this work, a poly(vinylidene fluoride) (PVDF)-based copolymer is synthesized by grafting two kinds of monomer, 2, 2, 3, 4, 4,-hexafluorobutyl methacrylate (HFMA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS), onto the PVDF powder with pre-irradiation grafting copolymerization. Then a new single lithium-ion conducting polymer electrolyte (SIPE) is prepared by solution casting of the radiation grafted PVDF-based copolymer powder with subsequent lithiation process. Its chemical structure, crystal form, and membrane morphology are characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM), etc. The mechanical properties exhibit the elongation at break of 72% and the tensile strength of 28 MPa. Comparatively high values of ionic conductivity, up to 2.08×10^{-5} S cm^{-1} at 30 °C, are obtained, combined with lithium-ion transference number of 0.93 and stable electrochemically oxidation voltage as high as 4.4 V vs Li/Li^{+}. Except for these promising features, the SIPE cell with lithium ion conduction network has a stable charge/discharge cycling performance with various C-rates at room temperature. As-prepared SIPE shows a great prospect for the application in lithium-ion batteries.

1. Introduction

The lithium-ion batteries (LIBs) have always attracted much attention with the rapid development of energy storages, portable electronic devices and electrical vehicles [1]. However, traditional organic solvent electrolytes now commercially used expose serious safety problems, which may suffer from leakage, degradation and flammability during charge/discharge process. Meanwhile, the conventional separators serve as the ionic conducting medium in LIBs, they possess many electrolyte-containing and interconnected pores, thereby, such that continuous pathways between cathode and anode will encourage the formation and growth of lithium dendrites during charging [2]. These dendrites reduce the battery's cycle efficiency and eventually cause a short circuit inside the cell. In recent years, the polymer electrolytes (PEs) as the important alternatives to liquid electrolytes used in LIBs have attracted significant interest, which act as a lithium ion migration medium as well as the separator to insulate cathode and anode materials [3,4]. Compared with traditional organic electrolytes, the PEs have the advantages of reducing the reaction with liquid electrolyte and good safety performance. At the same time, better shape flexibility and manufacturing integrity make thin-membrane electrolytes easily to process [4,5]. Since Wright et al. [6] reported firstly the conductivity of alkali metal ions with poly(ethylene oxide) (PEO) in 1973, there have been many efforts contributed to the PEs. A variety of polymers have been studied as a matrix, including PVDF [7], PEO [8], poly(methyl methacrylate) (PMMA) [9], polyacrylonitrile (PAN) [10] etc.

The pristine polymer matrix does not fully satisfy the application for the battery, which usually requires some modification [5]. Such as Liu et al. [11] prepared a polymer matrix membrane based on poly(acrylonitrilepolyhedral oligomeric silsesquioxane) (P(AN-POSS)). Although the PAN presents excellent film forming property and thermal stability, its high crystallinity and the strong polar groups $-C{\equiv}N$ weaken the ion conduction capacity and lithium-ion transference number (t_{Li+}). The introduction of polyhedral oligomeric silsesquioxane effectively reduced the crystallinity of PAN and improved t_{Li+}. Lee et al. [12] synthesized a cross-linked PVDF grafted copolymer as the polymer matrix of gel polymer electrolyte, while the chemical crosslinking method effectively avoids the loss of mechanical strength of PVDF due to liquid electrolyte immersion. It is worth noting that most of the PEs are dual-ion conductors, in which both anions and cations move simultaneously

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in electric field. When lithium ion is deposited or intercalated on cathode, the anion moves towards the anode and accumulates there [13]. A concentration gradient will set up next to the electrolyte, which results in the concentration polarization and the decrease of Li^+ transference number. It means that the real ionic conductivity of lithium ion is lower than the calculated value from data of electrochemical impedance spectroscopy. Most of dual-ion conductor electrolytes display a low t_{Li+} (0.3–0.5). In order to increase the conductivity, improve the output power and reduce the polarization loss, a concept of single ion conductor has been introduced in the PEs [14], which combines the anion of lithium salts with the polymer backbone and makes the t_{Li+} close to unit [13,15]. In recent years, it is an upsurge in the research of single lithium-ion conducting polymer electrolytes (SIPEs).

Armand et al. [16] reported an electrolyte by blending lithium poly (styrene trifluoromethanesulphonylimide of lithium) P(STFSILi) with PEO. Its ionic conductivity was 10^{-6} S cm^{-1} at 70 °C. Subsequently, they prepared a SIPE based on the self-assembled anionic ABA kind of triblock copolymers [17], where the A block was P(STFSILi), and the B block was PEO. The ionic conductivity increased to 10^{-5} S cm^{-1} at 60 °C, and the t_{Li+} was up to 0.85. The ionic conductivity of P(STFSILi)-PEO- P(STFSILi) increased by one order of magnitude with the increase of t_{Li+}. The immobilization of anionic groups on the main chain of the polymer is beneficial to the performance of LIBs. Ito and co-workers [18] prepared poly(ethylene oxide) oligomers with sulfonate groups on main chain ends. The ionic conductivity of SIPE was 4.45×10^{-6} S cm^{-1} at 30 °C and t_{Li+} was 0.75 at 20 °C. Porcarelli et al. [8] synthesized a ABA triblock copolymer electrolyte comprising PEO and poly(lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide) blocks. The value of ionic conductivity was further improved as high as 10^{-4} S cm^{-1} at 70 °C, with t_{Li+} of 0.91.

The PVDF is a most widely used polymer matrix for the PEs due to its excellent chemical and electrochemical stability [19]. In order to further improve the performance of PVDF as a matrix for the SIPE, the pre-irradiation grafting technology has been introduced to realize the anion fixation on the main chain. Herein, the radiation initiated graft copolymerization provides an alternative to highly incompatible polymers polymerization, while retains its inherent properties in the newly obtained copolymer. It is attraction of this method that it is convenient, simple and easy to control than general chemical copolymerization. And only by adjusting the composition and properties of monomers as well as reaction parameters, the polymer electrolytes tailored to the specific application system can be gotten [20,21]. The radiation grafting reaction is caused by a high-energy gamma ray, thus it is not necessary to add the initiator, and can gain the product with high purity [22]. In this work, we have designed a PVDF-based copolymer by grafting two kinds of monomer, 2, 2, 3, 4, 4,-hexafluorobutyl methacrylate (HFMA) and 2-acrylamido-2-methylpropanesulfonic acid (AMPS), onto the PVDF powder with pre-irradiation grafting copolymerization. Then a new SIPE was prepared by solution casting of the grafted copolymer powder with subsequent lithiation process. Besides to reduce the crystallinity of PVDF matrix by grafting it onto PVDF chain to form a block coploymers, HFMA is the fluorinated acrylate with high electron withdrawing fuorine atoms content, which is beneficial to the lithium ion dissociation and the chain segment motion [23]. The modification of HFMA monomer onto the copolymer is beneficial to the SIPE provides a higher charge carrier concentration. The 2-acrylamido-2-methylpropanesulfonic acid lithium (AMPSLi) has been grafted onto the PVDF as a lithium ion source for the polymer electrolytes [24]. The sulfonate and amide groups within AMPS make the copolymer have higher polarity, which is beneficial to the dissociation of lithium salts, and improves the ionic conductivity of the PEs [25]. The pure and uniform SIPE membranes prepared in this work exhibit remarkable comprehensive performances.

2. Experimental section

2.1. Materials

The 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate (HFMA, 96%) was purchased from Xeogia Fluorinesilicon Chemical Co., Ltd., China. The *N*-methyl-2-pyrrolidone (NMP, AR), methanol (AR), sodium hydroxide (AR), lithium hydroxide monohydrate (AR), ethylene carbonate (EC, AR), dimethyl carbonate (DMC, AR), *N*,*N*-Dimethylformamide (DMF, AR), hydrochloric acid (AR), and 2-Acrylamido-2-Methylpropanesulfonic Acid (AMPS) were all purchased from Aladdin, China. The PVDF was purchased from Songbai Chemical Co., Ltd., China. The HFMA was distilled under reduced pressure, and the PVDF was dried at 60 °C for 2 h under vacuum conditions before use. The NMP, EC and DMC were dried and stored in a glove box. The other chemicals were used as received.

2.2. Preparation of radiation grafted copolymer

The PVDF powder was pre-irradiated with the ^{60}Co γ-ray source to the total dose of 100 kGy at ambient temperature under argon atmosphere. Then the pre-irradiated PVDF power was stored at −40 °C for further use.

The pre-irradiated PVDF powder, HFMA and AMPS were mixed and dissolved in DMF solvent. The mixture was stirred and heated in an oil bath pan for 24 h in the case of nitrogen protection after vacuuming with double exhaust pipe. After the reaction, the solution was dripped into the precipitant under the condition of intense agitation, and the white particles were precipitated. Dissolved the sediment again and added the precipitant again. The above steps were repeated three times to remove the monomers and homopolymers in the copolymer. Finally, we got the pure radiation grafted copolymer named g-PVDF-H.

2.3. Preparation of SIPE membrane

The g-PVDF-H powder was added into DMF to form a 4 wt% evenly solution through magnetic stirring for 12 h. The g-PVDF-H membranes were formed in a glass plate and dried under vacuum at 60 °C for 24 h to remove the volatile solvents. In order to transform into "Li^+" type membranes, the g-PVDF-H membranes were soaked in calibrated 1 mol L^{-1} LiOH aqueous solution for 48 h. Finally, the lithiated membranes were washed by deionized water several times to fully remove the residual LiOH. Then the obtained SIPE membranes named g-PVDF-Li were further dried and stored in a glove box (Braun, $H_2O < 1$ ppm, $O_2 < 1$ ppm) prior to electrochemical tests.

2.4. Instrumentation and characterization

The structure of the PVDF and g-PVDF-H was conducted on the ^{1}H NMR (Bruker AV400) and FTIR (Nicolet iS5, Thermo Electron Corporation, USA). The crystal forms were analyzed by the XRD (MiniFlex/600, Rigaku Ltd.) at the scanning rate of 10° min^{-1} from 10° to 50°. The morphology of membranes was investigated by the SEM (Hitachi S-4800). The element distribution was analyzed by using energy dispersive spectral (EDS) combined with SEM. All samples were sputtered with platinum before testing in order to enhance the conductivity.

The quantitative acid-base back-titration was used to calculate ion exchange capacity (IEC). After immersing membrane into excess saturated NaCl solution for > 48 h, the H^+ in the solution originated from the membrane was titrated with calibrated 0.01 mol L^{-1} NaOH aqueous solution. Finally, the membranes were dried under vacuum for 24 h at 60 °C. The IEC is calculated as:

$$IEC = \frac{c \times V}{m}$$