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Application of poly(vinylidene fluoride-*co*-hexafluoropropylene) blended poly(methyl vinyl ether-*alt*-maleic anhydride) based gel polymer electrolyte by electrospinning in Li-ion batteries

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ABSTRACT

To compensate the disadvantage of traditional poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-HFP)) based gel polymer electrolyte (GPE) with poor rate performance, new GPE system consisted of P(VdF-HFP) and poly(methyl vinyl ether-*alt*-maleic anhydride) (P(MVE-MA)) with different ratios were prepared by electrospinning technology using polyethylene (PE) as support. After introducing P(MVE-MA) into P(VdF-HFP) system, the performance of the blended membrane and the GPE was significantly improved. Especially M4 based GPE blended with the mass ratios of P(MVE-MA): P(VdF-HFP) = 75: 25 exhibited the best physical and electrochemical characterizations. The developed membranes with interconnected fibrous structure showed the average diameter of 0.1–2.0 μm, which were facilitated for uptaking the liquid electrolyte and improving the ionic conductivity for corresponding GPEs. The introduced P(MVE-MA) copolymer presented higher decomposition voltage than P(VdF-HFP) copolymer from the calculation result of oxidation potential, leading to higher oxidative stability for blended GPE than pure P(VdF-HFP) based GPE. Furthermore, M4 based GPE presented remarkable interfacial compatibility with electrode and the lower polarization resistance, resulting in better cycling stability and rate performance, which had 96.5% capacity retention after 100 cycles and the discharge capacity at 5*C* kept 91.6% of 1*C* capacity in Li/GPE/$LiNi_{0.5}Mn_{1.5}O_4$ coin cell, compared with P(VdF-HFP) based GPE that had 87.8% retained capacity after 100 cycles and 48.7% retention capacity at 5*C*.

1. Introduction

Motivated by not only the superior energy density but also the promise of safer, lighter, and more flexible in shape during the commercial application, considerable efforts are currently put into the development of rechargeable lithium-ion batteries for such modern potable electronic devices and bendable electronic products as laptop computers, cellular phones and video cameras [1–5]. However, safety issues triggered by conventional carbonated organic solvent which is flammable and easy to ignite spontaneously on exposure in extreme condition such as high temperature, over-charging/discharge, have restricted the further development of lithium-ion batteries in emerging markets [6–8]. Thus, the alternative electrolytes attract attentions. Compared to the replacements of traditional liquid electrolyte with full solid-state electrolyte that possesses poor ionic conductivity at room temperature and pathetic interfacial compatibility between electrolyte and electorde, gel polymer electrolytes (GPEs) are taken into account as the most promising candidates of alternative electrolytes, which could solve the conflict between the safety deficiencies of liquid electrolyte and low ionic conductivity of solid electrolyte [9–13].

Usually, the GPEs composed of different polymer matrices with diversified chemical structures, such as polyethylene oxide (PEO), polymethylmethacrylate (PMMA), polyacrylonitrile (PAN), polyimide (PI), polyvinylidene fluoride (PVdF), poly(vinylidene fluoride-*co*-hexafluoropropylene) P(VdF-HFP) and etc., can merge the remarkable mechanical strength and lithium ion diffusion properties [14–20]. Among various polymeric matrix, P(VdF-HFP) is advantageous in lowering the crystalline and dimensional structure by interpenetrating hexafluoropropylene (HFP) amorphous phases into vinylidene fluoride (VdF) blocks, with the aim to modify the characteristic of the VdF

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homo-polymer, owing to the promotion of flexibility in copolymer chains which accelerates the transport of cations by its relatively high dielectric constant ($\varepsilon = 8.4$) [21–24]. However, gelation the carbonated liquid electrolyte into P(VdF-HFP) polymer matrix to form the P(VdF-HFP) based GPE still shows unsatisfied ionic conductivity and interfacial compatibility between high voltage cathode and the GPE [25–27]. Thus, it needs to improve the comprehensive performance of P(VdF-HFP) based GPE in order to further application the GPE in high energy density of lithium-ion batteries.

Interesting, poly(methyl vinyl ether-*alt*-maleic anhydride) (P(MVE-MA)) copolymer is usually used as substitute of medicine complication and drug carrier owing to its self-aggregation and complex stabilization of the polymer chain, which attributes to the outstanding mutual interaction established between polymer matrix and organic molecules [28]. In view of the high carrying capacity and the low release ability in plasma, P(MVE-MA) is chosen as the secondary phase to blend with P(VdF-HFP) in order to form the supra-molecular system aimed at the improvement in the performance of P(VdF-HFP) based GPE in this paper.

As one dimensional nanostructure materials, exquisite fibers have been subjective of intriguing application in membrane technology because of their unique properties. The traditionally interconnected porous membrane can be fabricated by multiple methods, such as immersed precipitation, preferential dissolution, solvent casting, phase transfer inversion, thermally induced phase separation, in situ polymerization and electrospinning [29–31]. Among the aforementioned approaches, electrospinning technology is a promising process of electrostatic interaction to produce consecutive polymer fibers with submicro fibers in the diameter range from about 5 μm to 200 μm, with the hope that are exceptionally long in length, uniform in diameter, and diversified in composition [32]. Due to the existence of adequately interconnected open porous structure, the electrospun membranes exert positive influence on providing more ionic transport channels and better specific surface area. The optimization of the processing parameters, for example, applied electric voltage, flow velocity of polymer fluid stream, solution composition, distance between spinneret needle and collector, ambient humidity of the chamber, should be intensive consideration to obtain the corresponding membranes with satisfied morphology and the better electrochemical characterization.

The main purpose of this work is to fabricate the intercross fibrous membrane by blending P(VdF-HFP) with P(MVE-MA) polymer matrix using electrospunning technology, to acquire the improved electrochemical performance of the GPE by combining the advantages of P(VdF-HFP) and P(MVE-MA). Additionally, polyethylene (PE) membrane is employed as support to assure the mechanical strength of the corresponding GPE. The characterizations of the membrane and the GPE are determined by physical and electrochemical methods, as well as quantum chemistry calculation.

2. Experimental

2.1. Preparation

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-HFP)) ((Mw: 400000, Sigma-Aldrich)) and Poly(methyl vinyl ether-*alt*-maleic anhydride) (P(MVE-MA)) (Mw: 216000, Aladdin) were purchased and used without further purification. Polyethylene (PE) (Celgard 2400, USA, thickness: 16 μm) membrane was used as support to prepare the PE supported blended membrane. According to the addition of P(MVE-MA) in the total weight with the concentration ranging from 0% (defined as M1), 25% (defined as M2), 50% (defined as M3), to 75% (defined as M4), the blended copolymer membranes were obtained by typical electrospunning method. We investigated the performance of M1–M4 membranes, because pure P(MVE-MA) membrane was difficult to prepare by electrospinning method since its slurry tended to form the droplet.

The homogeneous and viscous slurry with the concentration of 16 wt% was obtained by dissolving the P(VdF-HFP) and P(MVE-MA) copolymer into a mixed solvent (acetone/DMAc = 7:3 by weight) at room temperature after 1 h stir, and then stored in a capillary syringe pump using metal needle as solution reservoir [33–35]. The PE membrane located in a rotating drum was used to collect the copolymer fibers. The fibers were deposited on the tubular under the fabrication condition in the applied voltage of 18 kV and the distance between collector and tip of 20 cm at room temperature. The resulting fibrous membranes were further dried in vacuum at 60 °C for 12 h to complete evaporation of the solvent and water.

The corresponding GPEs were prepared by immersing the fibrous membranes in 1 M $LiPF_6$ liquid electrolyte solution using ethyl methyl carbonate (EMC), ethylene carbonate (EC) and diethyl carbonate (DEC) as solvent (EMC/EC/DEC = 5/3/2, in weight, from Dongguan Kaixin Materials Technology Co. Ltd., China) for 0.5 h.

2.2. Characterization

The surface morphology of microporous membrane was observed by a field-enhanced scanning electron microscope (SEM, JSM-6380LV, JEOL, Japan). The area diameter of the fibers was evaluated by SEM photograph based on a large magnification rate of 5000, using Nano-Measurer. The analysis of functional groups for the blended membranes were performed by Fourier transform infrared spectra (FTIR, Nicolet 6700, USA) in the wave number from 500 to 4000 cm^{-1}. The blended membranes were also measured by X-ray diffraction (XRD) apparatus using BRUKER D8 ADVANCE (Germany) with monochromatized Cu Kα radiation. The wetting performances of the membranes, involving the measurement of contact angles and the calculation of surface energy, were determined by the contact angle measurement instrument (JC2000D3P) at room temperature. The surface free energy was calculated by the method proposed by Owens [36]. The use of polar liquid (water) and non-polar liquid (*n*-hexadecane) to determine the surface energy leaded to a value equal to polarization and dispersion component of surface energy according to Eq. (1).

$$\gamma_L(1+\cos\theta) = 2(\gamma_S{}^D\gamma_L{}^D)^{\frac{1}{2}} + 2(\gamma_S{}^P\gamma_L{}^P)^{\frac{1}{2}} \tag{1}$$

where γ_L, γ_S were the surface energy, $\gamma_L{}^D$, $\gamma_S{}^D$, $\gamma_L{}^P$, $\gamma_S{}^P$ were the dispersion and polarization component of the liquid and solid, respectively.

In order to progress in comprehensive understanding the transfer behavior of lithium ion, the GPEs were assembled as symmetrical sandwiches between two stainless steel (SS) blocking discs in the structure of SS/GEP/SS. The ionic conductivity (σ) was determined by electrochemical impedance spectra (EIS) instrument (PGSTAT302N, the Netherlands) at ambient temperature with the applied potential amplitude of 10 mV as the commutable current signal and a range of frequency from 100 kHz to 1 Hz, which was calculated by Eq. (2).

$$\sigma = \frac{l}{RS} \tag{2}$$

where l was the thickness of GPE and S was the contact area between GPE and SS disc. The bulk electrolyte resistance (R) was determined by the intersection of the line composed of Nyquist plots with the real axis in EIS plots. The diameter of the stainless steel (SS) was 16 mm and the thickness of GPE was 54 μm averagely.

The electrolyte uptake ability ($A\%$) of the blended membranes was determined by immersing the fiber membranes in liquid electrolyte for a period of time, which was calculated through Eq. (3).

$$A(\%) = \frac{W_2 - W_1}{W_1} \times 100\% \tag{3}$$

where W_1 and W_2 were the mass of the dry and wet membranes, respectively.

The oxidative stability of the GPE was measured using linear sweep