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

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A B S T R A C T

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≡N weaken the ion conduction capacity and lithium-ion transference number (tLi⁺). The introduction of polyhedral oligomeric silsesquioxane effectively reduced the crystallinity of PAN and improved tLi⁺. 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.
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 PEIs [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 $t_{Li^+}$ 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 × $10^{-5}$ 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 containing PEO and poly(lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonylimide) 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 PEIs 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, 4-hexafluorobutyl methacrylate (HFMA) and 2-acrylamido-2-methylpropanesulfonic acid lithium (AMPSLi) has been sputtered with platinum before testing in order to enhance the conduction and characterization.

2. Experimental section

2.1. Materials

The 2, 2, 3, 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 powder 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$_2$O < 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 AV-400) 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:

\[
\text{IEC} = \frac{e \times V}{m}
\]
where the c and V represent the concentration and volume of standard NaOH solution consumed, respectively, and the m is the weight of the sample after drying. Based on the IEC formula, the degree of grafting (DOG) is calculated as:

\[ \text{DOG} = \text{IEC} \times M \times 100\% \]

where the M is molecular weight of the molecule.

The differential scanning calorimetry (DSC) measurement was conducted on a calorimeter (STA 449 F3 Jupiter Netzsch). The dried samples of 5–10 mg were placed in an Al2O3 pan and heated from 35 °C to 220 °C at 10 °C min \(^{-1}\) under a flow of Argon gas atmosphere.

The tensile tester (UTM, Instron Instruments) was used to test the mechanical properties of membranes with rectangular specimens (width: 2 cm; length: 5 cm; thickness: 30–60 μm). All tests were performed at 25 °C with a speed of 5 mm min \(^{-1}\).

The ionic conductivity of SIPE was measured by electrochemical impedance spectra (EIS) technique on an electrochemical workstation (Solartron SI 1287), from 0.01 Hz to 100 kHz with the voltage amplitude of 10 mV at open circuit potential. The SIPE membrane soaked up with the solution of EC/DMC (V:V = 1:1) was placed between two stainless steel electrodes. The device, SS|membrane|SS, was assembled and sealed in a glove box and was treated at 60 °C overnight. The electrochemical impedance spectra were recorded from 30 °C to 80 °C, and sealed in a glove box and was treated at 60 °C overnight. The tLi+ was measured by the CHI440B electrochemical workstation.

2.5. Battery assembly and measurement

To make a cathode, the LiFePO₄ acetylene black and the powder of g-PVDF-Li were dispersed in the NMP with the mass ratio of 8:1:1. The slurry was coated on an aluminum foil, vacuum-dried and cut into circular round with a diameter of 12 mm. The LiFePO₄ cathode, SIPE, and lithium foil were assembled at coin cells in a glove box (type 2016).

3. Results and discussion

The process for the preparation of SIPE is shown in the Scheme 1. The three major steps are listed as follows: (i) Pre-irradiation of PVDF powder. In argon atmosphere, PVDF is irradiated by gamma rays, and then polymer backbone forms active radicals. These active radicals have long life in low temperature and anaerobic environment. (ii) Grafting copolymerization preparation of grafted PVDF-based copolymer (marked as g-PVDF-H). Active radicals initiate the grafting process. The mechanism of grafting reaction is described in Fig. S1 (Supporting Information). (iii) SIPE membrane preparation with lithiation process (marked as g-PVDF-Li).

3.1. Structure, morphology and mechanical properties

\(^1\)H NMR spectroscopy was used to confirm the structure of pre-irradiation grafting copolymerization. In addition, NMR spectroscopy offers the possibility to indirectly calculate the grafting rate of HFMA and AMPS onto g-PVDF-H. Results are shown in the Fig. 1. All the samples except for AMPS have the peaks at δ = 3.34 and 2.50 ppm, which are due to water and solvent (DMSO-d₆). The AMPS monomer is extremely easy to absorb water, so a large amount of water molecules in DMSO-d₆ will shift the peak at δ = 3.34 ppm to a low field, and the peak area will increase. For the HFMA, the \(^1\)H NMR (400 MHz, DMSO-d₆) δ 6.34–6.02 (m, 2H), 5.88–5.77 (m, 1H), 4.81–4.61 (m, 2H), and 1.98–1.84 (m, 3H), ascribing to the hydrogen atoms on the HFMA monomer, are represented by ‘a’, ‘d’, ‘c’ and ‘b’, respectively. The integral ratio is 3:2:2:1, and agree with the target molecular structure. For the AMPS, the \(^1\)H NMR (400 MHz, DMSO-d₆) δ 8.37 (s, 1H), 6.02 (qd, J = 17.1, 6.1 Hz, 2H), 5.51 (dd, J = 9.8, 2.4 Hz, 1H), 2.79 (s, 2H), and 1.41 (d, J = 19.6 Hz, 6H), ascribing to the hydrogen atoms on the AMPS monomer, are represented by ‘g’, ‘e’, ‘f’, ‘i’ and ‘h’, respectively. The peak area ratio of the hydrogen atoms on the molecule is 2:1:1:6:1, and agree with the target molecular structure. The active hydrogen atom on -SO₄H is associated with DMSO solvent without peak at NMR, while the hydrogen atom on -NH- is not affected by solvent due to the shielding effect of (-C(H)₃)CH₂SO₄H group. The PVDF has two peaks at δ = 2.89 and 2.25 ppm which are attributed to the head-tail (H-T) > CH₃ protons and the tail-tail (T-T) > CH₃ protons [26,27]. In the Fig. 1 and Fig. S2 (Supporting Information), the g-PVDF-H shows peaks at δ = 8.23, 6.0 and 4.56 ppm corresponding to ‘g’, ‘d’ and ‘c’ hydrogen atoms, respectively, and the ‘a’, ‘b’, ‘e’, and ‘h’ hydrogen atoms appear at δ = 1.67–0.65 ppm. The peaks at δ = 2.68 and 2.45 ppm corresponding to ‘i’ and ‘f’ hydrogen atoms, respectively. It can be concluded from the \(^1\)H NMR results that the g-PVDF-H is successfully synthesized by the grafting process. Furthermore, in the \(^1\)H NMR spectrum of g-PVDF-H, the molar ratio of HFMA and AMPS is determined by the integral ratio of signal c and the signal g, and it is 4.61:1:7:05. Moreover, the ion exchange capacity of g-PVDF-H membrane is 0.48 mmol g⁻¹ according to the titration results. So combining integral ratio with IEC, as the hydrogen ions of these exchanges are derived from the AMPS molecule, the calculated DOG value of AMPS is 10.3% and the DOG value of HFMA is 6.9%.

The Fig. 2 shows the Fourier transform infrared spectroscopy of PVDF and g-PVDF-H powder. For the g-PVDF-H, the peak at 3345 cm⁻¹ is attributed to the -NH stretching vibration from the AMPS. The peaks at 1744 and 1664 cm⁻¹ are assigned to the C=O stretching of the acrylate groups and acrylamide groups, respectively [28,29]. It is further proved that two monomers of HFMA and AMPS are successfully grafted onto the PVDF molecule. The crystal forms of PVDF and g-PVDF-H power also determined by FTIR [30]. As the similar atomic radii of fluorine and hydrogen atoms, the PVDF exhibits various polymorphic structure [31]. The peaks at 976, 796, 764, 614 and 532 cm⁻¹ is observed in FTIR spectra of PVDF indicates that the crystal forms in PVDF are mainly the nonpolar α-phase corresponding to conformational sequences of TTTG [32]. The peaks at 510 and 467 cm⁻¹ is can be observed in the spectra, which indicates that the PVDF also contains fractional polar β-phase corresponding to conformational sequences of TTTT [33,34]. In the α-polymorph (TTTG), the distance between F and H is very close, so this structure makes it difficult for PVDF to interact with other molecules except itself. Moreover, the crystallinity of α-polymorph PVDF is high, then Li⁺ is hard to be transferred into the PVDF structure [35]. In the FTIR spectra of g-PVDF-H, it is interesting to find that the peaks at 976, 796, 764, 614 and 532 cm⁻¹ are weaken or even disappeared, while the peak at 510 and 467 cm⁻¹ are still strong. It can be concluded that the crystal forms of g-PVDF-H are mainly β-phase [36]. The transformation of crystal forms is caused by the interaction between carbonyl group and the fluoride group of PVDF [37]. The polar β-phase is a more attractive crystal type as a matrix for the PEs since it
shows a higher dielectric constant, which is beneficial to the dissociation of lithium salt and the forming of free lithium ions increasing the concentration of the charge carrier \cite{34,38}.

The X-ray diffraction directly characterize the crystal forms of PVDF and g-PVDF-H powder. In the Fig. 3a, the XRD peaks of PVDF located at 2θ = 18.3°, 19.94° and 26.6° show that the nonpolar α-phase is the dominated crystal forms \cite{39,40}. Compared with the PVDF, the diffraction peaks of g-PVDF-H at 18.3°, 19.94° and 26.6° disappear, while the diffraction peak of polar β-phase at 20.86° is the main diffraction peak \cite{41}. The XRD results are consistent with the FTIR results in the Fig. 2. The crystallinity (Xc) is calculated as:

\[
X_c = \frac{I_{cryst}}{I_{total}} \times 100\%
\]
where the melting enthalpy (\( \Delta H_f \)) of samples are obtained from the DSC curves, and the \( \Delta H_{100} \) is the melting enthalpy of perfectly crystalline PVDF (104.7 J g\(^{-1}\)) [42]. As shown in the Fig. 3b, the \( \Delta H_f \) of the PVDF and g-PVDF-H membrane are estimated to be 48.23 J g\(^{-1}\) and 43.69 J g\(^{-1}\), respectively. The reduction in \( X_c \) from 46.07% to 41.73% can be attributed to the copolymerization of the grating process to break the regularity of the polymer chain and thus the crystallinity degree is decreased [43].

The surface morphology images of the PVDF and g-PVDF-Li membranes observed with SEM are shown in the Fig. 4. The membranes are fabricated by solution casting method from the PVDF and the g-PVDF-Li powder, respectively. It can be identified that the PVDF membrane exhibits a typical spherical structure, while the g-PVDF-Li membrane has better compactness structure. The surface of g-PVDF-Li membrane has an uneven layer of overlapping lamellae with uniformly distributed micropores of size from 300 nm to 3 \( \mu \)m in diameter. The Fig. 4e is the EDS diagram of g-PVDF-Li membrane. It can be seen that the element N, O, F and S are evenly distributed in the membrane, and thus further proves that the membrane produced by pre-irradiation grafting copolymerization of the powder type base on PVDF is very uniform.

The manufacturability is one of the most important factors to be considered when battery technology moves from laboratory to full production [44]. The mechanical properties of the PVDF and g-PVDF-Li membranes are evaluated by a tensile test. The relationship between elongation at break and tensile strength is shown in the Fig. 5. The elongation at break of g-PVDF-Li membranes (72%) is much greater than that of the PVDF (19%). This is resulted from the bigger deformation space left in the g-PVDF-Li membrane compared with the PVDF membrane since the porosity of the former is higher than that of the latter [42]. Due to its better plasticity, the g-PVDF-Li membrane can be rolled or folded into a desired shape during the battery assembly.

### 3.2. Electrochemical performance

The ionic conductivity of SIPE with temperature change from 30 °C to 80 °C is shown in the Fig. 6. The result show that the ionic conductivity is \( 2.08 \times 10^{-5} \) S cm\(^{-1}\) at 30 °C. The ionic conductivity and temperature show a linear relationship in the temperature range, so the Arrhenius model is used for the treatment of the linear plot:

\[
\sigma = \sigma_0 \exp \left( \frac{-E_a}{RT} \right)
\]

where the \( \sigma_0 \) is a pre-exponential factor, and the \( R \) is the molar gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)). The \( \sigma \) and \( T \) refer to ionic conductivity and temperature, respectively. Inside, the ln \( \sigma \) and 1000/T reflect the activation energy of the ionic conduction (\( E_a \)), which represents the lowest energy required for ion transport in the electric field. The \( E_a \) value calculated from the linear fit result is only 1.72 kJ mol\(^{-1}\), which means that the ionic conductivity is not much influenced by temperature.

The electrochemical stability of the g-PVDF-Li electrolyte has been measured using cyclic voltammetry and linear sweep voltammetry, the results shown in the Fig. 7. In Fig. 7(a), two obvious peaks are found at

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\[
X_c = \frac{\Delta H_f}{\Delta H_{100}} \times 100\%
\]
−0.5 V and 0.38 V, they are corresponding to the process of lithium plating and stripping. The reversibility of lithium plating and stripping guarantees the high coulombic efficiency of the cell. In Fig. 7(b), the current onset is at about 4.4 V, and when the voltage gets higher, the current will change dramatically, indicating that the oxidation degradation begins. The occurrence of oxidative degradation is caused by the instability of SIPE at high potential. The result illustrates that the g-
PVDF-Li electrolyte is well suitable for the application in LIBs with 4 V cathode materials (LiFePO4).

The \( t^{\text{Li}^+} \) represents the proportion of carriers (Li\(^+\)) in electrical conduction. It is an important factor affecting the rate performance of lithium batteries. The steady-state current combined with electrochemical impedance spectroscopy determines the \( t^{\text{Li}^+} \). The g-PVDF-Li membrane soaked up with the solution of EC/DMC (V:V = 1:1) is placed between two lithium foils. The device, Li|SIPE|Li, is assembled and sealed in a glove box and is treated at 60 °C overnight. The \( t^{\text{Li}^+} \) is calculated as:

\[
\frac{I_{\text{ss}}}{I_0} = \frac{V}{R_f + R_i} \left( \frac{V}{R_o + R_s} \right)
\]

where \( V \) is the polarization voltage (3 mV), \( R_f \) and \( R_i \) are the body resistance and interface resistance of the electrolyte before and after polarization, \( I_0 \) and \( I_{\text{ss}} \) are the initial and steady state current, respectively [45]. From the Fig. 8, we can obtain the value of \( I_0 \) and \( I_{\text{ss}} \), and the fitted \( R_f \), \( R_i \), \( R_o \), \( R_s \) are 92.73 \( \mu \)A, 1.01 \( \mu \)A, 0.77 k\( \Omega \), 0.41 k\( \Omega \), 2.27 k\( \Omega \), 4.25 k\( \Omega \), respectively. So the value of \( t^{\text{Li}^+} \) is 0.93, close to unity, which is a typical for the SPIE. This result is consistent with the conclusion above, the structure of the g-PVDF-Li polymer is conducive to enhancing the Li\(^+\) migration. At the same time, anions are fixed in the main chain, limiting their long-distance motion, and Li\(^+\) is the only species that can migrate. In the flexible chain, HFMA, of polymer side chain, the F and O atoms have strong adsorption of electrons to facilitate the dissolution and separation of Li\(^+\). The result of the above common effect is that the g-PVDF-Li polymer electrolyte has a high \( t^{\text{Li}^+} \).

### 3.3. Battery performance

Compatibility of electrode and electrolyte greatly affect the performance of LIBs, especially that with the polymer electrolytes. To further investigate the electrochemical performance of the SPIEs used in an applicable cell, the g-PVDF-Li, as both binder and interfacial resistance reducer instead of the traditional PVDF binder, mixed with active material to fabricate the electrode. The EIS spectra of the coin cells with g-PVDF-Li and PVDF as the binders of the cathode material are shown in the Fig. 9. It can be concluded that the interfacial resistance and ionic transport resistance of the cell with the g-PVDF-Li binder are much smaller than those of the cell with the PVDF, which are beneficial to the ionic migration through the electrode/electrolyte interface and promoting the cell with improved electrochemical performance. The cycling performances of the cells with cathode used different binders are shown in the Fig. 10. The discharge capacity of the cathode with PVDF binder is much lower than that of the cathode with g-PVDF-Li binder. The degradation not only happens gradually along with the cycling, but also occurs with the rate increasing, which means that the cycling and rate performance is poor. Replaced the PVDF with the g-PVDF-Li, the battery cycle performance has been greatly improved.
improved. At 0.1C, the cell delivers a specific capacity < 140 m Ah g⁻¹ at the first few cycles, and then it reaches a stable value of about 142 m Ah g⁻¹. When the current density increases, a specific capacity of 133 m Ah g⁻¹, 118 m Ah g⁻¹ and 100 m Ah g⁻¹ can obtained at 0.2C, 0.5C and 1C, respectively. It should be pointed out that there is an activation process. The establishment of the lithium ion conduction network reduces the resistance in the cell and maximizes the utilization of active materials of electrode, which significantly improve the stable charge and discharge cycle of the battery, especially for the high rate cycling process.

4. Conclusions

The radiation initiated graft copolymerization is a convenient and simple way to realize the anion fixation on the main chain, even if two highly incompatible polymers are polymerized. In this study, a new type of SIPE based on PVDF prepared by irradiation grafting technology. The PVDF powder is modified with the AMPs and HFMA molecules, and both grafting lithium ion source and improving matrix properties are synchronously implemented. The AMPs molecules are immobilized on the main chain of PVDF, by which the Li⁺ is improved as high as 0.93. The highly investing electronic groups of −CF2 and −C≡O groups are beneficial to the lithium ion dissociation and further improvement of the ionic conductivity. With the grafting of AMPs and HFMA molecules onto PVDF, the crystal forms in g-PVDF-H are mainly the β-phase, which shows a higher dielectric constant and lower crystallinity. The g-PVDF-Li membrane has excellent mechanical properties with the elongation at break of 72% and the tensile strength of 28 MPa. Except for these promising features, the SIPE cell with g-PVDF-Li binder performs better cycling performance, because the lithium ion conduction network can reduce the resistance in the cell and maximize the use of active materials of electrode. According to the above conclusion, the SIPE membrane prepared by pre-irradiation grafting technology shows excellent comprehensive performance, which can be used in but not limited to the LIBs.

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Appendix A. Supplementary data

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