Novel Single Lithium-Ion Conducting Polymer Electrolyte Based on Poly(hexafluorobutyl methacrylate–*co*–lithium allyl sulfonate) for Lithium-Ion Batteries

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A new type of single-ion conducting polymer electrolyte for lithium-ion batteries, poly(hexafluorobutyl methacrylate-*co*-lith-ium allyl sulfonate) (P (HFMA-*co*-ASLi)), was firstly prepared by copolymerizing hexafluorobutyl methacrylate (HFMA) and so-dium allyl sulfonate (SAS) with a subsequent lithiation process. The prepared polymer electrolyte exhibits high lithium ionic conductivity (10^{-4} S cm⁻¹ at 80 °C) and excellent cycle perform-

1. Introduction

Much attention has been directed toward the application of lithium-ion batteries (LIBs) in portable electronic devices and hybrid electric vehicles in recent decades.^{[1],[2]} Higher energy density, lower cost and enhanced safety are becoming present main research directions. Great progress on the development of lithium-ion batteries based on conventional organic liquid electrolyte has been made over the last years.^[3] However, its potential safety problems cannot be ignored.^[4] Both carbonate solvents and lithium hexafluorophosphate degrade when stored at room temperature. As the temperature increases, this situation becomes more serious.^[5] The inflammable organic liquids are easy to leak and limited to high temperature use.^[6] Therefore, the quest for more reliable electrolyte is of great importance, and many researches have referred to polymer electrolytes.^{[7],[8]} In addition to the advantages of safety, polymer electrolytes are easier to design and processed into different forms.

Polymer electrolytes are usually prepared by mixing specific lithium salts with polymer skeletons, such as poly(ethylene oxide) (PEO),^{[9],[10]} polymethyl methacrylate (PMMA),^[11] polyacrylonitrile (PAN),^{[12],[13],[14]} polyvinylidene fluoride (PVDF),^{[15],[16]} poly (vinyl chloride) (PVC),^{[17],[18]} polyvinylidene fluoride-hexafluoro propylene (PVDF-HFP).^{[19],[20]} The key elements to evaluate

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 Supporting information for this article is available on the WWW under https://doi.org/10.1002/celc.201700256 ance at high temperature, which could be attributed to the good thermal stability (remains stable up to 300° C), mechanical properties (7.1 MPa for breaking strength) and high lithium-ion transference number (0.92). The electrolyte also displays good electrochemical stability (4.6 V). Our obtained results prove that the polymer P (HFMA-*co*-ASLi) is a promising candidate electrolyte for lithium-ion batteries.

polymer electrolytes are ionic conductivity, lithium-ion transference number, electrochemical stabilities, and so on.^{[21],[22]} One such issue arises from the fact that in many conducting polymer electrolytes, anions are easy to accumulate at the anode, leading to concentration gradient in the system, which results in low lithium-ion transference number $(0.3 \sim 0.5)^{[23]}$ and poor electrochemical performance.^[24] It has been reported that polymer electrolytes with a high lithium-ion transference number deliver better performance than those with a low lithium-ion transference number, even the ionic conductivity of the former is only one tenth of the latter.^[25] To cope with the problem, the most promising approach is to prepare single lithium-ion conducting polymer electrolytes (SIPE), which means the anions like carboxylate,^[26] sulfonate,^[27] sulfonyl imide,^[28] boron^{[29],[30]} centered and phosphorus^[31] centered anions are fixed on the polymer backbone through forming covalent bonds. Unlike the conventional dual-ion conducting polymer electrolyte, the only mobile species are lithium ions in the SIPE.^[32] The lithium-ion migration number of SIPE is close to unity and the SIPE can basically eliminate the concentration polarization and contribute to improving battery performance.

Armand et al.^[33] studied a multifunctional single lithium-ion triblock copolymer electrolyte based on poly(styrene trifluoromethanesulphonylimide of lithium)-poly(ethylene oxide)-poly (styrene trifluoromethanesulphonylimide of lithium) (P (STFSI-Li)-PEO-P(STFSILi)). The electrolyte contains a PEO segment and two polyanionic blocks, which could ensure mechanical performance and provide transferable lithium-ion source, respectively. Owning to the combined strong mechanical property and high lithium-ion conductivity, this BAB copolymer electrolyte exhibits a lithium-ion transport number higher than 0.85 and an ionic conductivity of $1.3 \times 10^{-5}\,\text{S\,cm}^{-1}$ at 60 $^\circ\text{C}.$ A kind of lithiated perfluorinated sulfonic polymer with short side chain was synthesized by Navarrini et al.^[34] and the corresponding lithium-ion exchange membrane was made through a meltpress method, while this work did not conduct further electrochemical property tests. In another related study,^[35] electro-



chemical properties of the previously cited lithiated perfluorinated sulfonic membrane were compared with the traditional separator with organic liquid systems, a higher capacity retention at high temperatures was realized and ionic conductivity of 4.63×10^{-4} S cm⁻¹ was achieved at ambient temperature. Wu et al.^[36] developed lithium polyvinyl alcohol oxalate borate (LiPVAOB), the ionic conductivity of the LiPVAOB membrane at ambient temperature was 6.11×10^{-6} S cm⁻¹ and its electrochemical window could reach 7 V (*vs.* Li⁺/Li), which could be applied to high-voltage lithium-ion batteries.

Herein, we have designed a novel single lithium-ion polymer electrolyte P (HFMA-co-ASLi). ASLi provides transferable lithium-ion source, Lewis base group in the flexible side chain of HFMA plays the role of solvation and desolvation. Fluoropolymer shows great electrochemical stability since the flexible side chain has a strong electron-withdrawing group (-C-F), which can also contribute to the dissolution and dissociation of alkali metal salts, thus making a proper delocalization of negative charges and providing higher carrier concentration. In addition, acrylate compounds have a good film-forming property, and the ester groups are favorable to improving the liquid absorption properties, thus enhancing the compatibility with carbonate-based solvent, which is of great importance to improving conductivity and cycling performance. The homopolymer of lithium allyl sulfonate is regular in structure and easy to form rigid structure, which is detrimental for ion conduction. When ASLi is copolymerized with HFMA via a simple one-step polymerization, advantages of the above two monomers can be integrated. Thence the simple one-step designed SIPE has outstanding thermal and electrochemical stability as well as high lithium-ion transference number. The primary results prove that the SIPE exhibits high lithium ionic conductivity and excellent cycle performance.

2. Results and Discussion

The copolymer electrolyte was prepared via a free-radical polymerization and a subsequent ion-exchange process, as shown in Scheme 1.

2.1. Structure Analysis

The structure of the copolymer was characterized by nuclear magnetic resonance (NMR) and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). Figure 1a shows ¹⁹F NMR spectra of the copolymers. As shown in the inset figure, three different kinds of fluorine atoms exist in the copolymer. The chemical shifts of the fluorocarbon are as follows. The absorption peaks of the CF₃ group appear in the low-field region at -75.21 ppm due to van der Waals effect, the absorption peaks of the CF₂ group is a little complicated due to the coupling of the $-OCH_2$ groups on the adjacent carbons, splitting into two peaks. The CHF does not have van der Waals effect, the absorption peak appears in the high field at 214.27 ppm. There is a consistent one-to-one match between

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 $\label{eq:scheme 1. Copolymerization of P (HFMA-{\it co-SAS}) and ion-exchange process to prepare P (HFMA-{\it co-ASLi}). Orange: fluoride ester flexible chain; blue: fixed anion; gold: Li^+.$



Figure 1. a) $^{19}{\rm F}$ NMR spectra of P (HFMA-co-ASLi). b) ATR-FTIR of P (HFMA-co-ASLi) SIPE membrane.

the ¹⁹F spectrum and the side chain units of HFMA,^{[37],[38]} indicating that the fluorine-containing monomer participated in the copolymerization. The ATR-FTIR results of copolymer and monomers are shown in Figure 1b and Figure S1 (Supporting Information). In the spectrum, the absorption peak at 1747 cm⁻¹ belongs to the stretching vibration of ester-bonded carbonyl (–C=O). The peak at 1234 cm⁻¹ refers to –C–O–C-vibrations. And the peak at 684 cm⁻¹ corresponds to the characteristic absorption peak of –C–F bond.^[39] The peaks at 1028 cm⁻¹ and 1188 cm⁻¹ correspond to symmetrical stretching vibration and antisymmetric stretching vibration of sulfonate,^[40] respectively. We can judge from the ATR-FTIR results that the



expected product with specific functional groups was obtained. It can be observed in Figure S1 the absorption peaks of -C=Care at 1640 cm⁻¹, no characteristic absorptions near 1640 cm⁻¹ appears in Figure 1b, indicating that there are no monomers in purified product.^[38]

2.2. Physical Properties

The weight-average molecular weight of the copolymer was determined by a standard laser light scattering (LLS) method as shown in Figure 2a. R_{θ} is Rayleigh ratio of solution at scattering



Figure 2. a) "Zimm plot" for P (HFMA-*co*-ASLi) in DMF at 25 °C. b) Strainstress curve of the SIPE membrane.(c) TGA thermogram and the corresponding DTG curve. d) DSC heating traces of the SIPE membrane.

angle θ ,K is a constant, c is concentration of the solution. The sample to be tested was dispersed in DMF. Step dilution method was used to determine the concentration of polymer solution. From "Zimm plot" in Figure 2a, we can get that $M_w = 1.04 \times 10^5$ g mol⁻¹. At the same time, we can know the radius of gyration ($R_g = 242$ nm) and the second Willy coefficient ($A_2 = 1 \times 10^{-4}$ cm³ mol g⁻²) from the calculated results. The molecular weight conforms to the requirements for self-standing film formation.

The mechanical property of SIPE membrane is very important for battery assembly. However, poor mechanical strength of the membrane lead to an internal short circuit. Figure 2 b shows the stress–strain curves of the SIPE membranes. It can be concluded that the breaking strength of SIPE membrane is 7.1 MPa and the elongation at break is 14.8%, which is acceptable for battery manufacturing processes. Thermal stability of the SIPE membrane is evaluated by the TGA method. The corresponding DTG curve is derived from the TGA curves shown in Figure 2c. From the DTG curve in Figure 2c, it can be observed that there is a major peak at 363 °C, which corresponds to the decomposition of main chain in the polymer. Slight weight loss (< 2.5%) before 300 °C is thought to be residual solvent. No significant weight loss is observed in our study before reaching the decomposition temperature of

300 °C, indicating that the SIPE membrane has good thermal stability. This attributes to the high chemical bonding energy of C-F (540 kJ/mol).^[41] From differential scanning calorimeter (DSC) curve in Figure 2d, there is an obvious change between $0^{\circ}C \sim 50^{\circ}C$. The onset of the heat capacity change appears at 17°C. We can draw the conclusion that 17°C corresponds to glass transition of the carbon chain. The average electrolyte uptake is calculated to be 40%. The ion exchange capacity (IEC) of SIPE is calculated according to titration results, and we can obtain that the average IEC value is 0.56 mmolg⁻¹. Based on IEC value, it can be calculated that C (wt. %) = 38.0, S (wt.%) = 1.7 and H (wt.%)=3.2, which is close to elemental analysis experimental values (wt.%): N (0.000), C (38.59), S (1.690) and H (3.460). The lithium ion content of SIPE membrane is conducted on an ion inductively coupled plasma-atomic emission spectroscopy (ICP-AES), the average content of lithium ions is 0.53 mmol g^{-1} .

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2.3. Morphological Characterization

The morphologies of the as-prepared SIPE membranes are investigated by a scanning electron microscope (SEM). Figure $3a \sim 3d$ show the photographs and microstructures of the



Figure 3. Photograph of SIPE membrane (a, b), surface and cross-section SEM images of the SIPE membrane (c, d), surface and cross-section EDS mappings (e, f) and EDS total element amount (g).

SIPE films. From Figure 3a and 3b, we can see that a transparent and flexible membrane is obtained. The microstructure of the surface of SIPE films is probed through SEM as depicted in Figure 3c. As we can see, the surface of SIPE is smooth and nonporous, which corresponds with the casting method of the membrane preparation. The appearance of cross-section of the membrane is presented in Figure 3d, the bulk of the SIPE membrane is dense as well, and the thickness of the SIPE membrane is approximately $60 \,\mu\text{m}$. Different from commercial porous polyolefin separators, the lithium-ion transport through SIPE membrane is dependent on the solvation and desolvation



of flexible segments rather than the pores of the separators. The surface and cross-section energy dispersive spectral (EDS) mappings are shown in Figure 3e and 3f. C, O, F, S are evenly distributed on the surface and cross section. Figure 3 g exhibits the EDS spectrograms of the total element amount information, the content of C, O, F, S element is consistent with the results of elemental analysis. The specific content of related elements are shown in Table S1(Supporting Information).

2.4. Electrochemical Performance

The typical electrochemical window of the SIPE membrane is measured using a linear sweep voltammetry at the scan rate of 0.1 mV s^{-1} with the EC/PC swollen SIPE membrane sandwiched between the lithium foil as the reference and counter electrode and the stainless steel sheet as working electrode at room temperature. The current changes at about 4.6 V as shown in Figure 4a, when scanning to higher potential, a sharp increase



Figure 4. a) Linear sweep voltammetry with a scan rate of 0.1 mVs⁻¹ (SS/ SIPE/Li). b) Polarization plots obtained by chronomaperometry ($\Delta V = 50$ mV). Inset in (b): Impedance spectra before and after the polarization process (Li/ SIPE/Li).

of current appears, indicating an oxidative degradation started. This result illustrates that the P (HFMA-*co*-ASLi) structure designed by us is stable for practical application in lithium-ion batteries. To determine lithium-ion transference number, the chronomaperometry results and the electrochemical impedance spectra before and after the polarization process are shown in Figure 4b. In the first few hundred seconds, the current drops sharply. As time goes on, the current is gradually close to a constant value, which is typical characteristic of the reduced concentration polarization in SIPE. Based on the electrochemical impedance combined with time-current method, the lithium ion transference number was calculated as follows [Eq. (1)]:

$$t^{+} = \frac{I_{s}(V - I_{0}R_{0})}{I_{0}(V - I_{s}R_{s})}$$
(1)

where I_0 and I_s represent the initial and steady-state current (measured by the time-current curve method), respectively. R_0 and R_s represent the initial and steady-state interfacial resistance of the passivation layer (measured by EIS), respectively. Vis polarization voltage step. The applied voltage is 50 mV. From Figure 4b we can obtain the value of I_0 , I_s and the fitted R_0 , R_s are 4.51 μ A, 3.88 μ A, 8.963 k Ω , 10.590 k Ω , respectively. The calculated t⁺ is 0.92. As the SO_3^- anions are fixed to the polymer backbone, their long-range movements are restricted, Li⁺ ions are the only movable species. Furthermore, Lewis base group in the flexible side chain of HFMA segments play the role of solvation and desolvation, F and O atoms on the side chains are favorable for the dissolution and dissociation of lithium salts owning to their strong electro-withdrawing effects, thus do help to the high lithium ion transference number.

The ionic conductivity of the membrane is a function of temperature, and as can be seen from Figure 5a, an increase by one order of magnitude is observed with temperature rising from $30 \,^{\circ}$ C to $80 \,^{\circ}$ C. The ionic conductivity of SIPE membrane is $1.68 \times 10^{-5} \, \text{S cm}^{-1}$ at $30 \,^{\circ}$ C and $1.44 \times 10^{-4} \, \text{S cm}^{-1}$ at $80 \,^{\circ}$ C, which can be mainly attributed to the better segment migration ability and higher ion diffusion with the temperature rising trend. The apparent activation energy (Ea) of lithium-ion transport is estimated from the Log σ vs. 1000/T curve in Figure 5b. The linear fit results illustrate that the ionic conductivity conforms to Arrhenius equation. The Ea is calculated according to Equation (2):

$$\sigma = \sigma_0 \exp\left(-Ea/RT\right) \tag{2}$$

where the σ_0 is pre-exponential factor and the R refers to the molar gas constant, 8.314 JK⁻¹ mol⁻¹. The Ea value has been calculated to be 40.83 KJ mol⁻¹.

To evaluate the cycling performance of the Li/SIPE/LiFePO₄ batteries, the cells are tested within the voltage range of 2.5 ~ 3.7 V (vs Li⁺/Li) at room temperature and 60 °C, respectively. As we can see from Figure 6a, the initial specific capacity is 122 mAh g⁻¹ and the initial coulomb efficiency is 90% at 25 °C, 0.2 C. After 80 cycles, the capacity retention maintains about 97.5%. When raising the temperature up to 60 °C, the first cycle discharge specific capacity could reach 163 mAh g⁻¹ at 0.2 C, and a cycle capacity retention of 97% is obtained after 80 cycles. The polarization during charging and discharging at a current rate of 0.2 C is obvious at room temperature due to the



Figure 5. a) lonic conductivity of the P (HFMA-*co*-ASLi) electrolyte. b) Arrhenius plots of the P (HFMA-*co*-ASLi) electrolyte.



Figure 6. a) Cycle performance of the SIPE membrane at 25 °C and 60 °C, 0.2C b) Charge and discharge voltage-capacity profiles of the first cycle at 25 °C and 60 °C, 0.2 C.

relatively low ion conductivity as shown in Figure 6b. The initial discharge capacity is 122.4 mAhg⁻¹, which is only 84% of the conventional liquid electrolyte (LE) batteries (145.1 mAhg⁻¹). When the temperature raised to 60° C, the initial discharge capacity can reach 162.9 mAh g⁻¹. This is due to the increased mobility of flexible polymer segments at high temperatures.

3. Conclusions

In this work, we disclose a new single lithium-ion conducting polymer electrolyte, P (HFMA-*co*-ASLi), which has been successfully prepared by the copolymerization of hexafluorobutyl methacrylate and sodium allyl sulfonate via free radical polymerization, followed by an ion-exchange process. Lithium allyl sulfonate provides anion-fixing groups and transferable lithium-ion source, Lewis base group in the flexible side chain of hexafluorobutyl methacrylate plays the role of solvation and desolvation.

The P (HFMA-*co*-ASLi) polymer electrolyte membrane was prepared by solution casting method. Structure of P (HFMA-*co*-ASLi) is confirmed through FTIR and NMR, and the average M_w is 1.04×10^5 g mol⁻¹, which satisfied the requirements of forming self-standing film. Thermal properties and mechanical behavior are studied as well. The P (HFMA-*co*-ASLi) membrane is stable up to 300 °C. The breaking strength is 7.1 MPa and elongation at break is 14.8%. The lithium-ion transference number is higher than 0.9. The electrochemical window can reach 4.6 V, and the ionic conductivity can reach 10^{-4} S cm⁻¹ at 80 °C, thus the battery made up with SIPE membrane exhibits excellent electrochemical properties during charge-discharge cycles at high temperatures. We believe that the P (HFMA-*co*-ASLi) electrolyte is a promising choice for lithium ion batteries in the future.

Experimental Section

Materials

The 2, 2, 3, 4, 4, 4-Hexafluorobutyl methacrylate (Xeogia Fluorinesilicon Chemical Co., Ltd., China) was purified before use. Sodium allyl sulfonate (SAS) and azodiisobutyronitrile (AIBN) (Aladdin) were recrystallized twice. LiFePO₄ was purchased from Ocell New Energy Technology Co., Ltd., China. The ethylene carbonate (EC) and propylene carbonate (PC) were dried and stored in a glove box. All the other reagents and solvents were purified by standard procedures before use according to respective requirements.

Preparation of Copolymer Electrolytes

HFMA and SAS were added to a four-necked flask equipped with a thermometer, a magnetic stirring bar and a reflux condenser. The radical initiator was AIBN, and the reaction temperature was 65 °C. After reacting for 12 h, the product was precipitated several times to get purified. The copolymer was dried at 80 °C for at least 12 h to obtain P (HFMA-*co*-SAS).



Preparation of SIPE Membrane

The SIPE membrane was made through solution-casting method. P (HFMA-*co*-SAS) was fully dissolved in DMF to prepare a 5 wt.% solution, the solution was cast on a flat plate, followed by vacuum-drying for 12 h before heating to remove the remaining bubbles and then drying for 24 h at 60 °C in vacuum. The cast membrane was placed into a 0.5 mol/L H₂SO₄ solution for 48 h at 25 °C, fresh H₂SO₄ solution was replaced every 6 h. After that, deionized water was used to wash the membrane till neutral. The membranes were immersed in saturated Li₂CO₃ solution at 25 °C for 48 h, replaced with fresh Li₂CO₃ solution every 6 h, washed with deionized water, and dried at 80 °C for 24 h. The obtained P (HFMA-*co*-ASLi) membranes were transferred into a glove box for later use.

Instrumentation and Characterization

All procedures that related to dealing with moisture or oxygen sensitive reagents were performed under conditions of a dry argon atmosphere, or in a glove box (Braun, $H_2O < 1$ ppm, $O_2 < 1$ ppm).

The Bruker AV400 NMR spectrometer was used to record ^{19}F (470 MHz) spectra of the copolymer. Purified samples were fully dissolved in deuterated tetrahydrofuran. Further structure characterization of the as-synthesized copolymer was conducted on ATR-FTIR (Nicolet IS5, Thermo Fisher Scientific Corporation, USA) in the wavenumber between 600 cm $^{-1}$ and 4000 cm $^{-1}$.

The weight-average molecular weight (M_w) was determined by a normal laser light scattering (LLS) spectrometer (BI-200SM) outfitted with a Mini-L30 diode laser (532 nm) as the light source at 25 °C. LLS is an absolute method to measure M_w . The measurable range is $1 \times 10^4 \sim 1 \times 10^7$ g/mol.

The mechanical properties of the SIPE membrane were tested through universal testing machines (UTM, Instron Instruments). According to the standard plastics-determination of tensile properties for films (GB/T 13022–91), the extension rate was kept at ~1.66 mm s⁻¹. The size of the polymer sheet tested was ~2 cm× 5 cm×50~70 μ m (width×length×thickness).

The thermal gravimetric analysis (TGA) was conducted to test the thermal stability of membranes (STA 449 F3 Jupiter Netzsch). $5 \sim 10 \text{ mg}$ dried samples were placed in an Al₂O₃ pan and heated from 35 °C to 800 °C at 5 °C min⁻¹ under a flow of Argon atmosphere. The thermal decomposition temperature (T_d) was defined as the sample lost its 5% weight. T_g of the SIPE was studied on a DSC (Netzsch 200 F3). Sample of an average weight of $5 \sim 10 \text{ mg}$ was sealed in an Al₂O₃ pan, then cooled and heated at a rate of 20 °C min⁻¹ from -150 °C to 150 °C under a nitrogen flow rate of 30 mL min⁻¹. T_g (the onset of the heat capacity change) was recorded during the cooling and heating process.

Quantitative acid-base back-titration analysis was used to calculate IEC of the membrane. The specific operation of acid-base titration analysis is as follows. At first, the electrolyte membrane was converted to an acid form. The P (HFMA-*co*-ASLi) membrane was immersed into H_2SO_4 (1 mol/L) solution at room temperature for 2 days, replacing fresh solution every 6 h. After that, we washed the membrane several times with deionized water and dried in the vacuum oven. We could get the Na⁺ form membrane by immersing the original acid-form membrane into excess saturated NaCl solution for more than 48 h. The H⁺ in the solution originated from the membrane was titrated with calibrated 0.01 mol/L NaOH aqueous solution. Finally, the membrane was dried under vacuum for 24 h at 60 °C. We calculate the IEC according to the following equation [Eq. (3)]:

$$IEC \ (mmol \ g^{-1}) = (V_{NaOH} \times c)/m_{drv}$$
(3)

where the m_{dry} is weight of the final dried "Na⁺" form membrane, the c and V represent the concentration and volume of NaOH aqueous solutions, respectively.

The electrolyte uptake of the membranes was measured by comparing the weight difference between the dry and solvent-saturated membranes. The solvent-saturated membrane was prepared by immersing the dried membrane into ultrapure EC/PC (V:V = 1:1). We measure the weight of the membrane after wiping off of free liquid on the surface until there was no weight change, named as m_{wet} . The dried membrane, named as m_{dry} . The electrolyte uptake was calculated by Equation (4):

Electrolyte uptake
$$(\%) = (m_{wet} - m_{dry})/m_{dry} \times 100\%$$
 (4)

The surface and cross section appearance of the SIPE membrane were investigated with SEM (Zeiss Sigma, Germany). The element distribution was analyzed by using SEM combined with EDS (Oxford X–MAX). The samples to be observed cross section morphologies were fractured through liquid nitrogen freezing process. All samples were sputtered with platinum before testing in order to enhance the conductivity.

The element analyses were performed on an Vario EL (Elementar Analysen System GmbH, Germany) elemental analyzer.

To reveal the exact lithium content of the SIPE membrane . we used ICP-AES to detect the content of lithium ions of SIPE membrane. A certain weight of P(HFMA-*co*-ASLi) membrane sample was soaked in a certain volume of HCI solution for 72 h at 80 °C to realise a sufficient ion exchange.

The electrochemical window measurement was conducted on an electrochemical workstation (CHI440B) at 25 $^\circ$ C between 2~5.5 V.

Lithium-ion transference number (t⁺) of SIPE was obtained by the steady-state current method combined with electrochemical impedance spectroscopy(EIS), using a CHI440B electrochemical workstation and Solartron electrochemical workstation respectively. The electrodes were sandwiched between two lithium foils, and the appropriate amount of electrolyte (EC/PC = 1:1 by volume) was added to prepare a Li|SIPE|Li symmetric cell system. EIS was conducted from 0.01 Hz to 100 KHz with a voltage of 5 mV and fitted with equivalent randles circuit. Steady-state current method was carried out with a polarization voltage of 50 mV for 10,000 seconds. The measurement was performed at a constant temperature of 25 °C.

Electrochemical impedance spectra (EIS) technique was used to calculate the ionic conductivities (σ) of SIPE, which was conducted on an electrochemical workstation (Solartron SI 1287). The frequency ranged from 0.01 Hz to 100 kHz. SIPE soaked in EC/PC (V:V = 1:1) were sandwiched between two stainless-steel electrodes. Before measuring, the cell was treated at 60 °C for 6 h to create better contact between the electrolyte and electrodes. The Electrochemical impedance spectra were recorded over the temperature in the range of 30 °C to 80 °C. σ is calculated from the previously obtained resistance by the equation of σ =L/(S×R_b), where L represents the thickness of the membranes, S is the area of the specimen, and R_b represents bulk resistance. R_b is obtained through the fit of equivalent circuit model.

To test the electrochemical performance of cells assembled with the EC/PC swollen SIPE, the coin cells (type 2016) were assembled by sandwiching the membrane between $LiFePO_4$ cathode and lithium foil in a glove box. The $LiFePO_4$ cathode was made by



spreading a mixture of 80 wt. % grinded LiFePO₄ powder, 10 wt.% as-prepared P (HFMA-*co*-ASLi) binder and 10 wt. % conductive additive (acetylene black) onto an aluminum foil.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrochemical performance · lithium-ion batteries · polymer electrolytes · transference number

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