

Synthesis and Characteristics of a Silicon-Containing Polymer, Manufacture of an Electrolyte Membrane from the Polymer and Poly(vinylidene fluoride-co-hexafluoropropene), and Property Testing of the Membrane

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ABSTRACT: A silicone-containing polymer was synthesized by addition polymerization between 1,12-bis(3-methyl-3-oxetanyl)-2,5,8,11-tetraoxadodecane and dichloride dimethylsilane catalyzed by tetrabutylammonium bromide and was characterized by Fourier transform infrared spectroscopy, ¹H-NMR, gel permeation chromatography, and differential scanning calorimetry analyses. To manufacture a tough solid electrolyte membrane, various amounts of a poly(vinylidene fluoride-co-hexafluoropropene) copolymer was used to reinforce this silicone-containing polymer. The mechanical properties and compatibility of the resulting membranes were assessed by mechanical testing and

scanning electron microscopy observation. The ionic conductivity was assayed from an alternating-current impedance spectrum. The results reveal that the maximum ionic conductivity reached 7.4×10^{-5} S/cm at 30°C and 2.6×10^{-4} S/cm at 80°C, respectively. Additionally, the linear sweep voltammetry tests showed that this kind of the blended polymer electrolyte was electrochemically stable until 4.3 V. The thermogravimetric analysis measurements also implied its good thermal stability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1086–1093, 2009

Key words: addition polymerization; blending; silicones

INTRODUCTION

Since the pioneering work of Wright and Armand was reported in 1970s,^{1,2} solid polymer electrolytes (SPEs) have attracted immense interest for their potential applications in lithium-ion batteries. Because of their high safety performance and solid characteristic, SPEs are very promising as a replacement for the liquid electrolytes used in pocket lithium cells and make it possible to manufacture various kinds of novel lithium cells, such as powerful cells for electric vehicles and tiny cells with optional shapes.^{3–5} However, they have not been practically applied in lithium cells to date because of their lower ionic conductivity. Hence, a great deal of work is still needed to improve the ionic conductivity of SPEs.

Recently, siloxanes have been used to prepare silicone-containing polymer electrolytes with improved ionic conductivity, which arises from their flexible backbones and lower glass-transition temperatures compared with the polyethers currently used in polymer electrolytes.^{6,7} In addition to the higher ionic conductivity, these silicone-containing polymers usually possess a better thermal stability than those polyethers because of the fact that the bond energy of the Si–O bond is stronger than that of C–O.^{8,9} Thus, both the safe performance and ionic conductivity are anticipated to be simultaneously improved through the incorporation of siloxanes into the polymer electrolyte matrices.

It was reported that an addition polymerization can occur between four-membered oxetane rings and chloride silanes in the presence of onium salts.^{10–12} In this study, a bisoxetane compound, 1,12-bis(3-methyl-3-oxetanyl)-2,5,8,11-tetraoxadodecane (TrDOE) was first prepared by the attachment of oxetane to the both ends of triethylene glycol. Then, a novel silicone-containing polymer was synthesized by addition polymerization between TrDOE and dichloridedimethylsilane catalyzed by tetrabutylammonium bromide (TBAB). However, the molecular weight of this silicone-containing polymer

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was found to be low, and its mechanical properties were not strong enough to form a good self-standing membrane.^{10–12} The copolymer poly(vinylidene fluoride-*co*-hexafluoropropene) (PVdF–HFP) is a popular matrix material used in gel polymer electrolytes, and a very high ionic conductivity is attained when it is combined with a liquid electrolyte to form a gel.¹³ Although the higher mechanical properties of a silicone-containing polymer can be approached by increasing the molecular weight through chemical processes such as chain extending and crosslinking, such processes are very complex and difficult to control. Alternatively, the blending process was the method of choice in this study.

To this end, the as-synthesized silicone-containing polymer was blended with PVdF–HFP copolymer to manufacture good self-standing polymer electrolyte membranes. The silicone-containing polymer was responsible for the ionic conduction, and the PVdF–HFP copolymer was amenable for the improvement of the mechanical properties.

EXPERIMENTAL

Materials and measurement

PVdF–HFP copolymer, lithium trifluoromethanesulfonimide (LiTFSI), and tetraphenylphosphonium bromide (TPPB) were bought from Aldrich (Milwaukee, WI) and were used as received. Dichloridedimethylsilane was purchased from Shanghai Chemical Reagent Co. (Shanghai, China), and TBAB was purchased from Beijing Chemical Reagent Co. (Beijing, China). Dichloridedimethylsilane was distilled, and TBAB was recrystallized in ethyl acetic ester before use. All other reagents were purchased elsewhere.^{14,15}

Fourier transform infrared (FTIR) spectra were measured with a Shimadzu (Kyoto, Japan) IR Prestige 21 instrument. ¹H-NMR spectra were recorded on a Varian Mercury Plus 400 (Palo Alto, CA) with CDCl₃ as a solvent containing TMS as an internal standard. Gel permeation chromatography (GPC) analysis was made on a Waters (Milford, MA) 2414 with three Waters Styragel HMW columns at 35°C with tetrahydrofuran (THF) as an eluent. Elemental analysis was carried out on a Vario EL III (Hanau, Germany). A Shimadzu E-60 differential scanning calorimeter was used for analysis of the thermal behavior of the polymers at a heating rate of 10°C/min. Scanning electron microscopy (SEM) observation was carried out on Hitachi (Tokyo, Japan) S-4800 scanning electron microscope. Thermogravimetric analysis (TGA) was conducted on a TGA 2000 thermogravimeter (Waltham, MA).

Synthesis of TrDOE

The synthesis of 3-hydroxymethyl-3'-methyloxetane (HMO) was reported previously.^{16,17} A toluene solu-

tion (150 mL) containing 75.6 g (0.396 mol) of *p*-toluenesulfonyl chloride and 6.44 g of TBAB was added to a three-necked, round flask and vortexed under mechanical stirring. An aqueous solution of sodium hydroxide (71.2 g, 35%) was slowly added, and the mixture was cooled to 10°C. Triethylene glycol (27.2 g, 0.181 mol) was added dropwise for 1 h and stirred in excess of 4 h to gradually form a white precipitate. Then, HMO (44.6 g, 0.437 mol) was slowly added to the reaction mixture, and the grains of sodium hydroxide (34.7 g, 0.868 mol) were added in excess of 1 h. The mixture was stirred at 60°C for 1 h and finally refluxed for an additional period of 4 h. After distilled water (300 mL) was added to dissolve the sodium chloride precipitates, the mixture was extracted successively with toluene (300 mL). The extract was washed twice with distilled water (200 mL) and dried with anhydrous sodium sulfate. The solvent was removed, and the remaining liquid was distilled twice *in vacuo* at 170–180°C to give 17.8 g of the TrDOE product.

Yield = 30.9%. FTIR (cm⁻¹): 1113 (C–O), 978 (oxetane's C–O–C). ¹H-NMR (ppm): 1.28 (6H, CH₃), 3.51 (4H, OCH₂–C), 3.61–3.63 (12H, CH₂CH₂O), 4.30–4.47 (8H, oxetane's CH₂). ANAL. Calcd: C, 60.36%; H, 9.43%. Found: C, 59.81%; H, 9.59%.

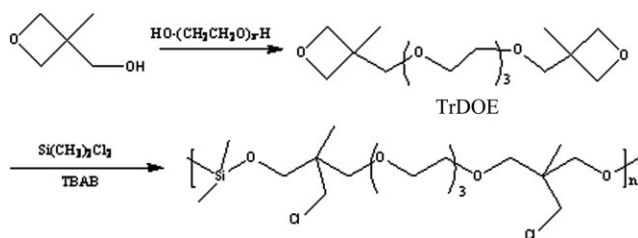
Polymerization

TBAB (0.16 g) was dissolved in 5 mL of toluene under ultrasonication for 15 min and mixed with 3.18 g (0.01 mol) of TrDOE. The mixture was added to a dry round flask under a N₂ atmosphere. Then, 5 mL of a toluene solution of dichloridedimethylsilane (1.29 g, 0.01 mol) was introduced into the flask dropwise at 0°C for 1 h under a N₂ atmosphere. The reaction temperature was increased to 60°C and kept for 30 h. The catalyst was washed with distilled water and dried with anhydrous magnesium sulfate. The solvent was then removed by rotation evaporation and dried *in vacuo* to give a sticky product.

Yield ≈ 95%. FTIR (cm⁻¹): 1110 (C–O), 1053 (Si–O), 725 (C–Cl). ANAL. Calcd (under the assumption that the enchainment ratio of TrDOE to dichloridedimethylsilane was 1 : 1): C, 48.31%; H, 8.11%. Found: C, 48.19%; H, 8.01%.

The ¹H-NMR spectra of the silicone-containing polymer were recorded on a Varian Mercury Plus 400 with CDCl₃ as a solvent containing TMS as an internal standard. The NMR results are discussed hereinafter.

The polymer sample was first dissolved in THF at a concentration of about 5 mg/mL. Then, GPC measurements were carried on a Waters 2414 with three Waters Styragel HMW columns at 35°C with THF as an eluent. From the GPC results, the molecular weight was determined as calibrated with polystyrene standards.



Scheme 1 Synthesis route for the monomer and addition polymerization.

A Shimadzu E-60 differential scanning calorimeter was used for analysis of the thermal behavior of the polymers at a heating rate of 10°C/min. The polymer samples (6–10 mg) were heated from –100 to 100°C in stainless steel pans. The results of the second run were used for the glass-transition temperature investigation.

Preparation and characterization of the blended polymer electrolyte membrane

Predetermined amounts of the silicone-containing polymer, PVdF–HFP copolymer, and LiTFSI were dissolved in 2 mL of THF. The solution was then poured into a plate, and the solvent was vaporized under a N₂ atmosphere to form a self-standing polymer electrolyte membrane. The membrane was dried *in vacuo* for the following mechanical tests and electrochemical measurements.

The mechanical properties were measured by a DXLC-5000 mechanical testing machine manufactured by Shanghai D&G Measure Instrument Co., Ltd. (Shanghai, China). A 1-kN load cell was used for these materials. The samples were cut into dumbbell shapes, which provided a gage length of 20 mm and a width of 4 mm. The specimens were pulled at a rate of 100 mm/min, and the results reported are the mean values for five replicates.

The membrane samples were cut from large mats and then sputter-coated with gold in preparation for the SEM tests. The SEM picture of each blend polymer membrane sample was taken at 2000× magnification.

The TGA measurement was conducted from 50 to 600°C under a N₂ atmosphere at a heating rate of 10°C/min. The samples were placed in a vacuum oven at 100°C overnight to ensure that they were completely free of moisture. During the TGA–FTIR measurement, the FTIR spectra were collected at intervals of 10 s.

Electrochemical tests

After the preparation of the polymer membrane, it was transferred to a glovebox filled with argon and placed for 24 h to remove possible moisture and oxygen in the surface of the membrane. Then, the cell for electrochemical tests was assembled in the glovebox.

The ionic conductivity was measured via alternating-current (ac) impedance analysis with an electrochemical cell consisting of the electrolyte film sandwiched between two blocks of stainless steel. The ac impedance analysis was performed with a CHI 660A electrochemistry station made by Chen Hua Instrument Co. (Shanghai, China). The measurements were carried out from 30 to 80°C with an interval of 10°C. The conductivity (σ) was calculated as follows:

$$\sigma = l / (R_b \times A) \quad (1)$$

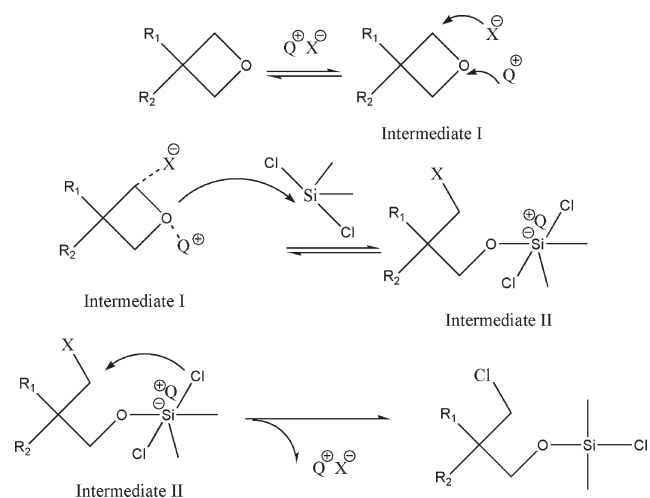
where R_b is the bulk resistance from ac impedance, l is the film thickness, and A is surface area of the electrode.

The linear sweep voltammogram measurement was performed with a two-electrode cell, where the polymer electrolyte was sandwiched between the lithium and copper foils. The cell was assembled in the MBRAUN glovebox filled with argon. The measurement was carried out on the CHI 660A electrochemistry station from open-circuit voltage to 5 V, and the sweeping rate was 5 mV/s.

RESULTS AND DISCUSSION

Synthesis and characterization of the silicone-containing polymer

The synthetic route of the silicone-containing polymer is shown in Scheme 1. As reported,^{11–13} the oxetane ring could react with Si–Cl bond in the presence of the quaternary onium salt. The proposed reaction mechanism is shown in Scheme 2. Intermediate I was formed from the reaction of oxetane with TBAB as a catalyst. It further reacted with dichloridodimethylsilane to yield intermediate II. After that, it decomposed automatically to produce a 1 : 1



Scheme 2 Proposed mechanism for the addition reaction between oxetane and dichloride dimethylsilane.

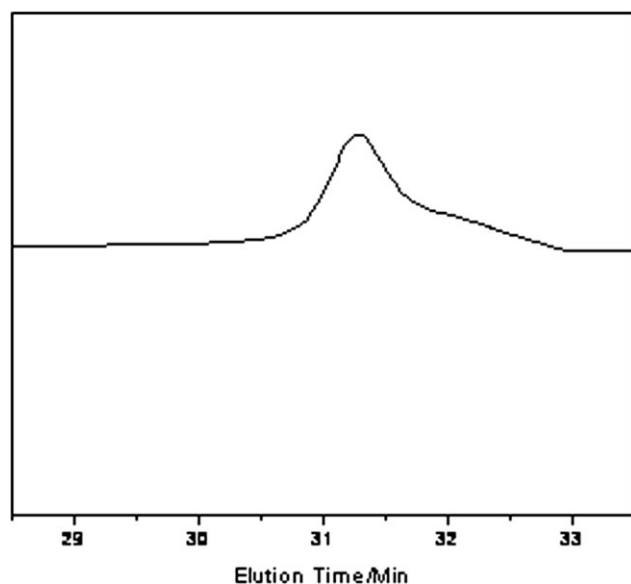


Figure 1 GPC trace of the silicone-containing polymer.

product and release the catalyst.¹⁰ Evidently, if difunctional monomers, such as TrDOE and dichloridedimethylsilane, are used, an addition polymerization product can be obtained under the conditions that an exact stoichiometric 1 : 1 ratio of reactive groups of the two monomers is strictly kept.

A series of experiments were carried out to determine suitable polymerization conditions. First, TPPB and TBAB were used to catalyze the polymerization, respectively. However, the solubility of TPPB was much lower than that of TBAB in most of organic solvents. As a result, only TBAB was chosen as the catalyst for synthesizing the silicone-containing polymer. Second, toluene was chosen as the solvent because it dissolved TBAB and other reactants more smoothly compared with the other solvents. Third, after a series of polymerizations were performed at

various temperatures, 60°C was chosen over the other temperatures because of the maximum yield of the product at this temperature.

A typical GPC trace of the silicone-containing polymer is shown in Figure 1. Its number-average molecular weight was determined to be about 4000 with a nearly symmetrical and unimodal peak, which indicated that the addition polymerization indeed proceeded.

Figure 2 shows the ¹H-NMR spectrum of the target polymer. The resonance peak at 0.08 ppm was assigned to the methyl group connected to the Si atom, whereas that at 0.93 ppm corresponded to the methyl group in the TrDOE component. The ratio of the integral areas of the two resonance peaks was just equal to 1 : 1, which was consistent with the theoretical proton ratio of the two types of methyl groups in the two monomers in the polymer. This result also matched the data of elemental analysis and implied that the composition ratio of two repeat units in the copolymer was 1 : 1.

In addition to the two peaks mentioned previously, a group of peaks at 3.38–3.67 ppm were ascribed to the methylene group in the polymer. However, it was difficult to distinguish these resonance peaks because they had very close chemical shifts and heavily overlapped each other.

Additionally, two groups of small peaks at 4.31–4.50 ppm were assigned to the methylene group of the oxetane ring of TrDOE in the terminal structure. Similarly, there were also two small peaks around 0.08 and 0.93 ppm, which corresponded to the terminal methyl group in TrDOE and the dichloridedimethylsilane moieties, respectively. Consequently, the degree of polymerization could be calculated by the following equation:

$$A_T/A_C = 1/(n + 1) \quad (2)$$

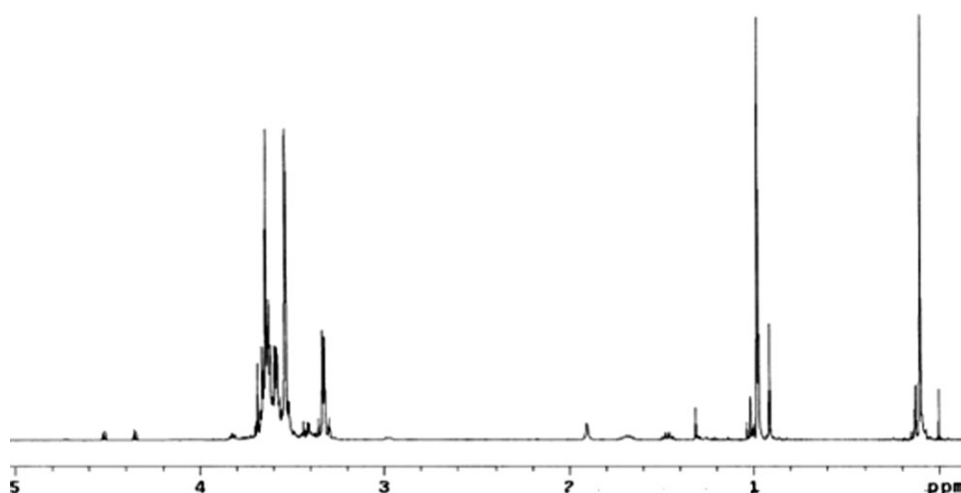


Figure 2 ¹H-NMR spectrum of the silicone-containing polymer.

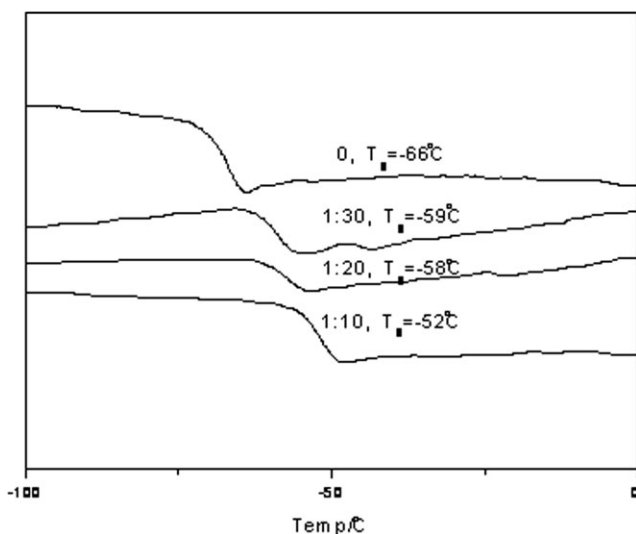


Figure 3 DSC curves of the silicone-containing polymer with various feed ratios of LiTFSI to oxygen atoms in the polymer (the molar ratios of 0, 1 : 10, 1 : 20, and 1 : 30 are the feed ratios of LiTFSI to oxygen atoms in the polymer of the corresponding DSC curve).

where A_T and A_C represent the integral area of the terminal Si—CH₃ and the integral area of the main-chain Si—CH₃, respectively, and n represents the degree of polymerization (not including terminal groups). Accordingly, the number-average molecular weight was obtained from the degree of polymerization data. It was found to be about 2900, which was lower than that evaluated by GPC analysis.

Differential scanning calorimetry (DSC) thermograms of the silicone-containing polymer blended with and without LiTFSI are shown in Figure 3. As shown, the glass-transition temperature (T_g) of the polymer increased with increasing molar ratio of lithium salt to oxygen atoms in the polymer. However, with doping with LiTFSI or not, T_g was obviously lower than in those polyethers generally used in SPE, for example, poly(ethylene oxide), poly(propylene oxide), and the comblike polyether that was synthesized in our previous study.¹⁷ Hence, this silicone-containing polymer would benefit the enhancement of ionic conductivity.

Preparation of the polymer electrolyte membranes

The silicone-containing polymer was blended with 30–70 wt % PVdF–HFP to form a series of self-standing membranes. When the PVdF–HFP content was below 30 wt %, the membrane became sticky and was easily broken up. It seemed that at least 40 wt % PVdF–HFP copolymer was needed for a good self-standing membrane.

The mechanical properties of these blended membranes with PVdF–HFP contents ranging from 40 to 100 wt % were measured, and the results are illus-

trated in Figure 4. The mechanical strength of the blended polymer electrolyte membranes was evidently enhanced by the addition of PVdF–HFP copolymer. Furthermore, the tensile strength of the blend polymer electrolyte membrane containing 80 wt % PVdF–HFP was higher than the one containing 100 wt % PVdF–HFP. This phenomenon indicated good compatibility between the PVdF–HFP copolymer and the silicone-containing polymer. However, as the polymer electrolyte membrane, each blend membrane needed some lithium salts added. For the pure PVdF–HFP membrane, its tensile strength may have been weakened because of the existence of 5 wt % lithium salt. Because the silicone-containing polymer had both good compatibility with the PVdF–HFP copolymer and good solubility with lithium salts, the tensile strength of the PVdF–HFP membrane was spontaneously strengthened after blending with a 20 wt % silicone-containing polymer compared with that of the pure PVdF–HFP membrane added with 5 wt % lithium salt.

The SEM pictures of the blended membranes with various PVdF–HFP contents are shown in Figure 5. As shown, there was basically one continuous phase, which indicated good compatibility between PVdF–HFP and the silicone-containing polymer. However, the surface morphology shown in Figure 5(a,b) was smooth and tight, which led to a higher tensile strength. On the contrary, the surface morphology shown in Figure 5(c,d) was concavoconvex and loose, which gave a lower tensile strength.

Ionic conductivity measurements

Figure 6 shows the ionic conductivity plots versus various PVdF–HFP contents. The ionic conductivity increased with decreasing PVdF–HFP content. The

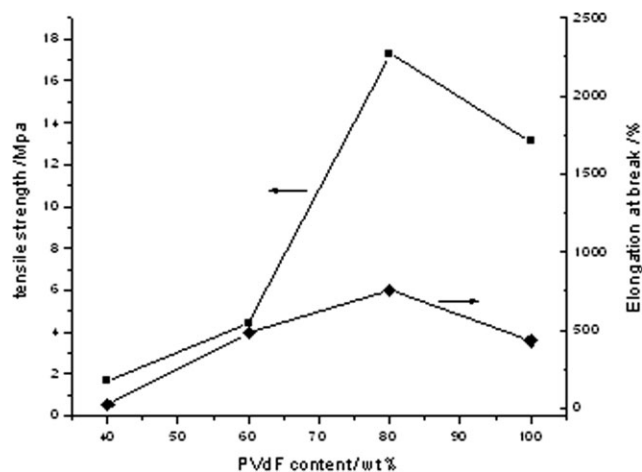


Figure 4 Mechanical properties of the blended polymer electrolyte containing 5% LiTFSI.

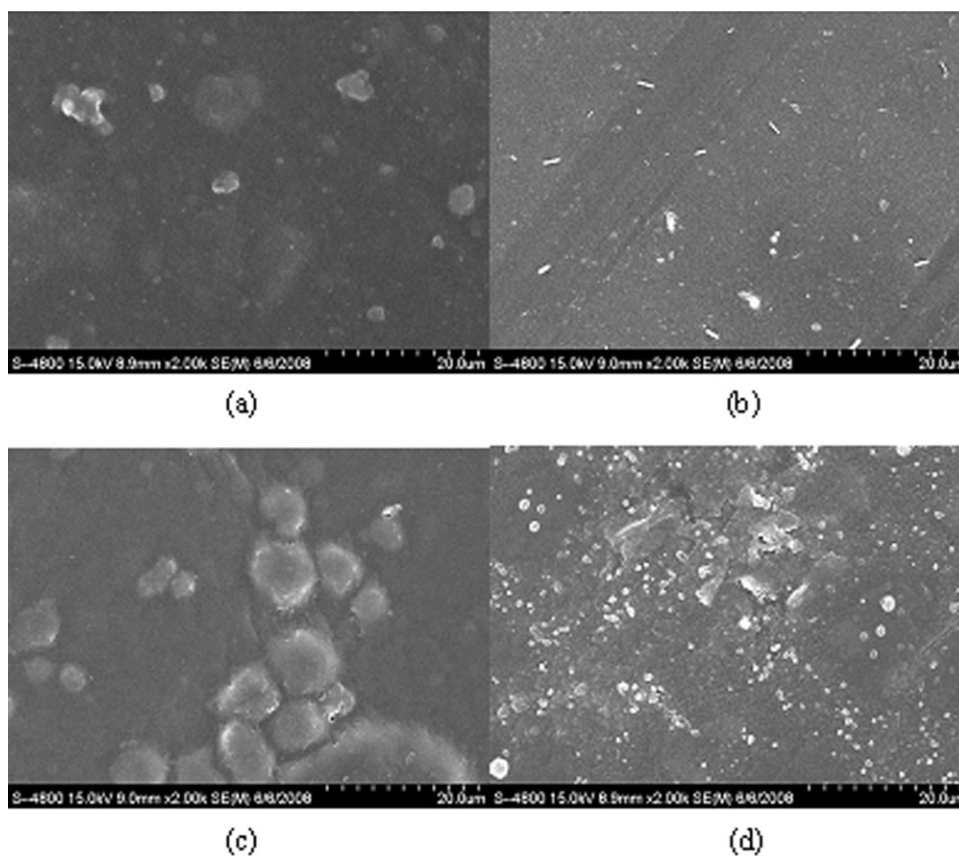


Figure 5 SEM pictures of the blended polymer electrolyte containing 5 wt % LiTFSI: (a) 100, (b) 80, (c) 60, and (d) 40 wt % PVdF-HFP.

polymer electrolyte containing 30 wt % PVdF-HFP imparted ionic conductivity to a magnitude of 7.4×10^{-5} S/cm at 30°C and 2.6×10^{-4} S/cm at 80°C, respectively. The addition of the PVdF-HFP copolymer contributed greatly to the dimensional stability of the silicone-containing polymer electrolyte. However, the blending certainly affected the ionic conductivity because PVdF-HFP was hardly capable of complexing with lithium ions to facilitate ionic transportation.¹⁸ For the tradeoff of ionic conductivity and mechanical properties, an optimal PVdF-HFP content in the blends was determined to be 40 wt %. As a result, a blended polymer electrolyte membrane with 40 wt % PVdF-HFP was used in the following electrochemical and thermal stability measurements.

Figure 7 displays the ionic conductivity comparison for the polymer electrolyte with and without blending with the PVdF-HFP copolymer at two lithium salt concentrations. The ionic conductivity of the silicone-containing polymer electrolyte reinforced with PVdF-HFP was obviously lower than that of the pure silicone-containing polymer electrolyte. The ionic conductivity of the silicone-containing polymer decreased nearly half a magnitude after the addition of 40 wt % PVdF-HFP copolymer. This suggested

that further research work, such as increasing the molecular weight of silicone-containing polymer, is needed because the ionic conductivity can be improved by decreasing the content of PVdF-HFP

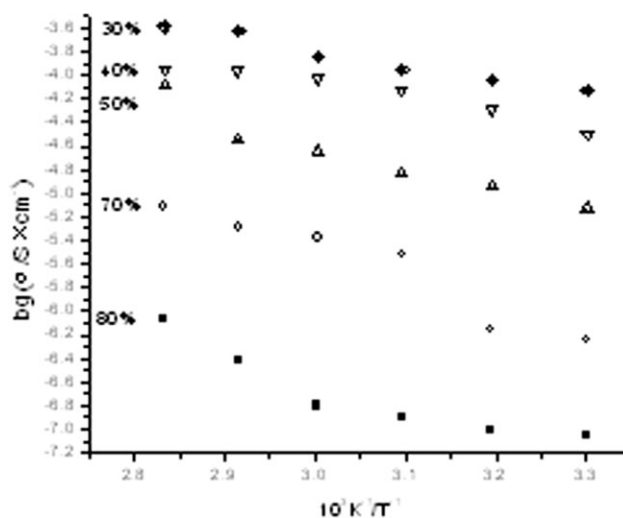


Figure 6 Ionic conductivity versus various PVdF-HFP contents (each with 5 wt % LiTFSI).

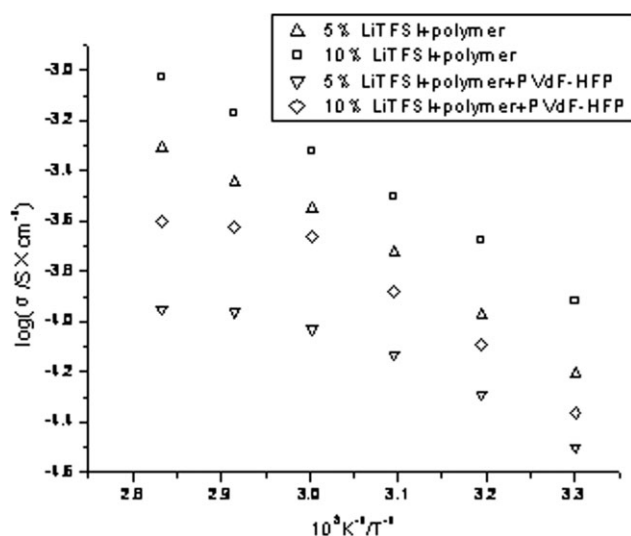


Figure 7 Ionic conductivity plots of the polymer electrolyte with and without blending with the PVdF-HFP copolymer.

copolymer or completely eliminating it in the blended polymer electrolyte.

Electrochemical stability of the blend polymer electrolyte membrane

As shown in Figure 8, the electrochemical stability window was tested for the blended polymer electrolyte. The current–voltage response (linear sweep voltammetry) was recorded by the construction of a cell where the blended polymer electrolyte was sandwiched between Li and Cu electrodes. The flat of current flow was taken as the electrochemical stability window for this blended electrolyte. As shown in Figure 8, the polymer electrolyte was stable to 4.3 V,

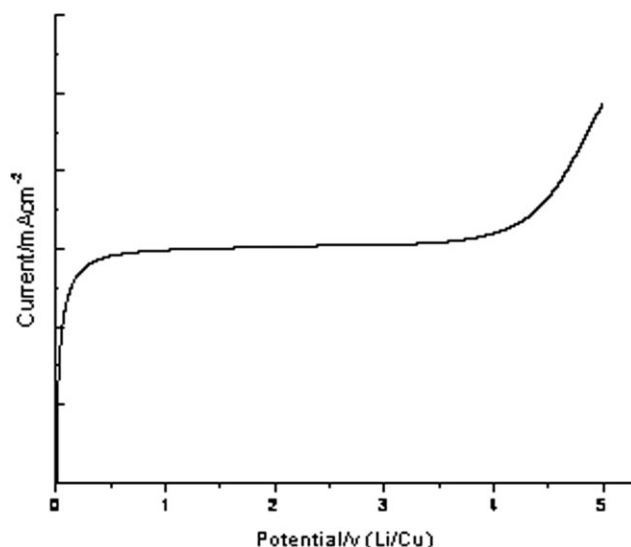


Figure 8 Linear sweep voltammetry of the blended polymer electrolyte containing 10 wt % LiTFSI.

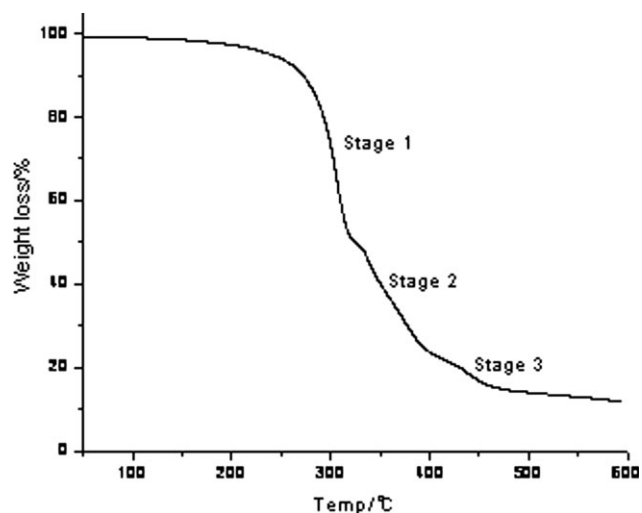


Figure 9 TGA curve of the blended polymer electrolyte containing 10 wt % LiTFSI.

which in principle, meets the requirement of lithium-ion batteries.

Thermal stability of the blend polymer electrolyte membrane

The thermal decomposition processes of the resultant blended polymer electrolytes are shown in Figure 9. The sample started to lose weight around 285°C, and the weight loss was completed at over 500°C. This decomposition temperature was substantially higher than that of the liquid electrolytes currently used in lithium-ion batteries.¹⁹ Compared with their liquid counterparts, the weight-loss process of this blended SPE was gradual and slow. Accordingly, if used in lithium-ion batteries, they would certainly be more thermostable than liquid electrolytes.

In addition, we found here that three stages occurred in the weight-loss process for the blended SPEs. To understand the decomposition process, the decomposition products were measured by TGA-FTIR measurement, as shown in Figure 10. The three spectra were measured at the midpoint of three stages, respectively. However, the PVdF-HFP copolymer may have given off fluoride-containing gases such as HF during the decomposition process, whereas the silicone-containing polymer would have been likely to give off H₂O and CO₂, as the silicone would have been present in the form of residue. The gas products, including H₂O and CO₂, could be seen in first stage's spectrum,²⁰ whereas in the spectra of both the second and third stages, the resonance peak assigned to HF was found.²¹ Hence, we concluded that the first decomposition stage, starting at about 285°C, may have involved the decomposition of the silicone-containing polymer, and the second and

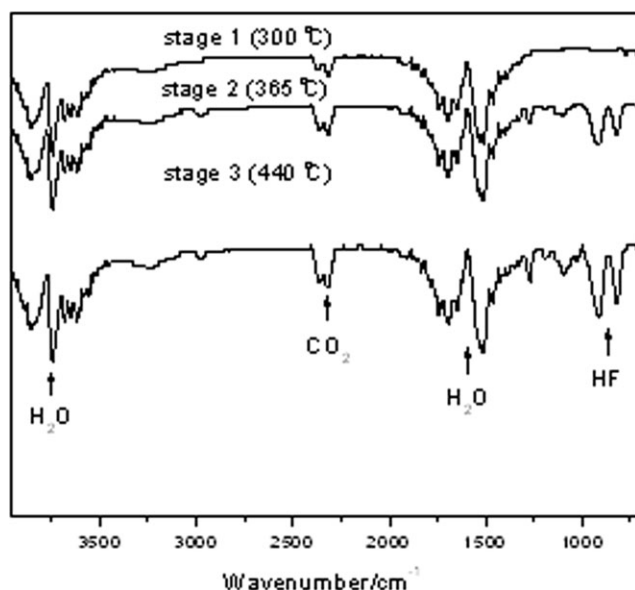


Figure 10 TGA-FTIR spectra of the blended polymer electrolyte.

third stages, beginning at about 330 and 430°C, respectively, were most likely related to the decomposition of the PVdF-HFP copolymer.

CONCLUSIONS

A silicone-containing polymer was synthesized by addition polymerization between TrDOE and dichloride dimethylsilane. Subsequently, a kind of SPE membranes was prepared by blending with PVdF-HFP. The ac impedance measurement indicated that the maximum ionic conductivity reached 7.4×10^{-5} S/cm at 30°C and 2.6×10^{-4} S/cm at 80°C after blending with 30 wt % PVdF-HFP. However, for the tradeoff of ionic conductivity and

mechanical properties, the optimal PVdF-HFP content in the blend was 40 wt %. Linear sweep voltammetry showed that the blended polymer electrolytes were stable up to 4.3 V. Meanwhile, TGA implied good thermal stability of these blended polymer electrolytes.

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