Preparation and Characterization of Proton Conducting Composite Membranes From P(VDF-CTFE)-*g*-PSPMA Graft Copolymer and Heteropolyacid

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Abstract: Proton conducting composite membranes were prepared by solution blending of poly(vinylidene fluoride-*co*-chlorotrifluoroethylene)-*graft*-poly(sulfopropyl methacrylate) (P(VDF-CTFE)-*g*-PSPMA) graft copolymer and heteropolyacid (HPA). The P(VDF-CTFE)-*g*-PSPMA graft copolymer was synthesized by atom transfer radical polymerization (ATRP) using direct initiation of the secondary chlorines of P(VDF-CTFE). FT-IR spectroscopy revealed that HPA nanoparticles were incorporated into the graft copolymer via hydrogen bonding interactions. The water uptake of membranes continuously decreased with increasing HPA concentration up to 45 wt%, after which it slightly increased. It is presumably due to the decrease in number of water absorption sites due to hydrogen bonding interaction between the HPA particles and the polymer matrix. The proton conductivity of membranes increased with increasing HPA concentration up to 45 wt%, resulting from both the intrinsic conductivity of HPA particles and the enhanced acidity of the sulfonic acid of the graft copolymer.

1. Introduction

Polymer electrolytes comprise metal salts of low lattice energy dissolved in a polymer matrix containing polar moieties such as ether, ester, or amide linkages. Metal salts can dissolve into such polymer matrices by virtue of the coordinative interaction between the metal ion and the polar groups. This type of polymer electrolyte has received great attention for the applications to electrochemical devices such as lithium rechargeable batteries, dye-sensitized solar cells or facilitated olefin transport membranes [1-4]. Another type of polymer electrolyte is polyelectrolyte possessing negatively charged sulfonic acid groups. This class of materials has been extensively investigated for the applications to fuel cells during the last decade [5-8].

The most common proton conducting polymer electrolyte membranes are based on perfluorinated membranes, such as the Nafion series from DuPont and the Aciplex series from Asahi Chemical. All of these membranes possess good thermal, chemical, and mechanical properties because of their perfluorinated polymer backbones. However, high cost, low proton conductivity, and low water uptake at high temperatures are the main obstacles for the commercialization of polymer electrolyte membranes for fuel cells. Therefore, significant research efforts have been devoted to the development of alternative sulfonated polymeric materials [9-13]. Among them, an organic-inorganic composite material with nano-size interfaces between organic and inorganic domains offers exceptional opportunities to create novel polymer electrolyte membranes with unique properties [14-21].

In this study, we synthesized poly(vinylidene fluoride-*co*-chlorotrifluoroethylene)-*graft*-poly(sulfopropyl

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methacrylate) (P(VDF-CTFE)-*g*-PSPMA) graft copolymer by atom transfer radical polymerization (ATRP) using direct initiation of the secondary chlorines of P(VDF-CTFE) and then blended with HPA at various weight ratios. The hybrid organic-inorganic nanocomposite membranes were characterized in terms of proton conductivity and water uptake.

2. Experimental

2.1. Materials

P(VDF-*co*-CTFE) (PVDF SOLEF® 31508/1001) was kindly provided by Solvay., 3-sulfopropyl methacrylate (SPMA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 99%), copper (I) chloride (CuCl, 99%), heteropolyacid (HPA, phosphotungstic acid, $H_3[P(W_3O_{10})_4]$) were purchased from Aldrich. HPA was dried at 100°C in an air circulating oven for overnight before use but others were used as received without further purification.

2.2. Synthesis of Graft Copolymer

In a 50 mL vial, 14 g of SPMA was dissolved in 54 mL of DMSO at 70°C. In 250 mL round bottom flask, 2 g of P(VDF-CTFE) was dissolved in 28 mL of NMP at 70°C. The SPMA solution was added to the P(VDF-CTFE) solution. Then 0.04 g of CuCl and 0.1 mL of HMTETA were added to the solution. The green mixture solution was stirred until homogeneous solution and purged with nitrogen for 20 min. The mixture solution was placed in a 90°C oil bath for 24 hr. After passing the solution through a column with activated Al_2O_3 to remove the catalyst, it was precipitated into methanol. The polymer was purified by redissolving in DMSO and reprecipitating in methanol. P(VDF-CTFE)-*g*-PSPMA copolymer was obtained and dried in a vacuum oven overnight at room temperature.

2.3. Preparation of Composite Membranes

The composite membranes containing HPA in various weight ratios were prepared using a solution cas-

ting method. First, the as-synthesized P(VDF-CTFE)-*g*-PSPMA graft copolymer was soaked in methanol at 40°C for 1 h. Then it was soaked in 0.5 N H_2SO_4 at room temperature for 15 h. The proton-exchanged graft copolymer was thoroughly washed with deionized water. It was then dried in a vacuum oven at room temperature for 24 h. The acidic graft copolymer and the desired amount of HPA at 15, 30, 45, 60 wt% of HPA concentration were dissolved in DMSO together to form a transparent solution. After complete dissolution, the polymer solutions were cast onto a Teflon-coated glass dish. The solutions were dried in a convection oven at 80°C for 48 h, and then in a vacuum oven at 100°C for 24 h.

2.4. Water Uptake

Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent paper to remove the excess of water adhering to it and the sample was then weighed. The water uptake of the membrane was determined from

$$\text{water uptake (wt\%)} = \frac{W_w - W_d}{W_d} \times 100 \tag{1}$$

where W_w and W_d are the weights of wet and dried membranes, respectively.

2.5. Proton Conductivity

A four-point probe method was used to measure the proton conductivity of the membranes. Before the measurement of proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range 1 Hz ~ 8 MHz at 25°C, using a ZAHNER IM-6 impedance analyzer. The impedance spectra of the membranes can be used to generate Nyquist plots, and the proton conductivity was calculated from the plots [22].
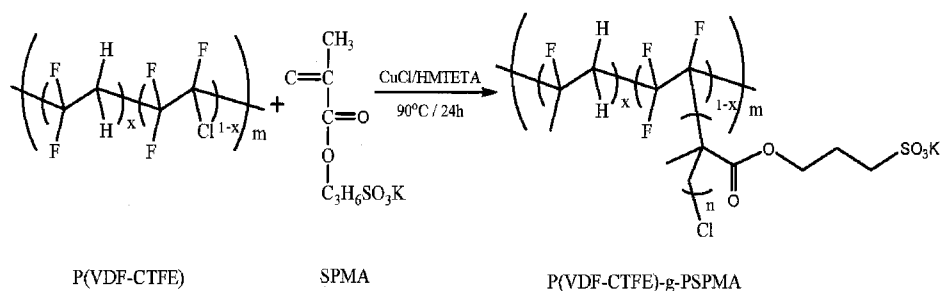
**Scheme 1.** Synthetic procedure for P(VDF-CTFE)-g-PSPMA graft copolymer via ATRP.

2.6. FT-IR Spectroscopy

FT-IR spectra of the samples were collected using Excalibur Series FTIR (DIGLAB Co.) instrument between the frequency range of 4,000 to 600 cm^{-1} using ATR facility.

3. Results and Discussion

The schematics for the synthesis of P(VDF-CTFE)-g-PSPMA graft copolymer electrolyte is shown in Scheme 1. P(VDF-CTFE) backbone was directly grafted with styrene sulfonic acid (SSA) at 90°C for 24 h through ATRP technique. The amphiphilic P(VDF-CTFE)-g-PSPMA graft copolymer is expected to molecularly self-assemble into continuous nanophase domains of semicrystalline P(VDF-CTFE) interweaved with hydrophilic proton conducting domains of PSPMA brush layer, providing a mechanism for facile proton transport through the membranes.

Fig. 1 presents the FT-IR spectra of P(VDF-CTFE) and P(VDF-CTFE)-g-PSPMA graft copolymer synthesized by ATRP. Compared to pristine P(VDF-CTFE), the strong absorption band at 1,716 cm^{-1} was observed in P(VDF-CTFE)-g-PSPMA, assigned to the carbonyl bond of ester group. The strong band centered around 1,160 cm^{-1} is presumably due to the overlap of the asymmetric stretching vibration of sulfonic acid group and C-O bond of ester group. The P(VDF-CTFE)-g-PSPMA graft copolymer also exhibited the strong absorption band at 1,180 cm^{-1}, resulting from stretching vibration of sulfonate groups [23]. The broad absorption band at around 3,435 cm^{-1} is attributed to the
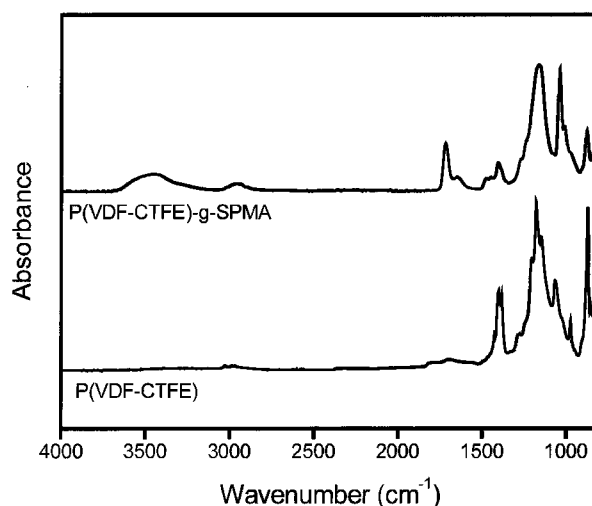

Fig. 1. FT-IR spectra of pristine P(VDF-CTFE) and P(VDF-CTFE)-g-PSPMA graft copolymer.

water bounded to ionic groups of the membranes. These FT-IR spectroscopic results also support the successful graft copolymerization via ATRP from secondary chlorine atoms on the P(VDF-CTFE) backbone.

Scheme 2 shows the preparation method for composite polymer electrolyte membranes by blending P(VDF-CTFE)-g-PSPMA and HPA. The FT-IR spectra of pure HPA, P(VDF-CTFE)-g-PSPMA graft copolymer and P(VDF-CTFE)-g-PSPMA/HPA composite membrane with 30 wt% of HPA were measured and presented in Fig. 2. The typical vibrations of HPA molecules were observed at 1,075, 974, 908 and 804 cm^{-1} for neat HPA, which are the stretching vibrations of P-O, W = O$_t$ (O$_t$ is the terminal oxygen), W-O$_c$-W (corner-shared octahedral) and W-O$_e$-W (edge-shared octahedral) [18].

P(VDF-CTFE)-g-PSPMA   PWA

Composite P(VDF-CTFE)-g-PSPMA/PWA membrane
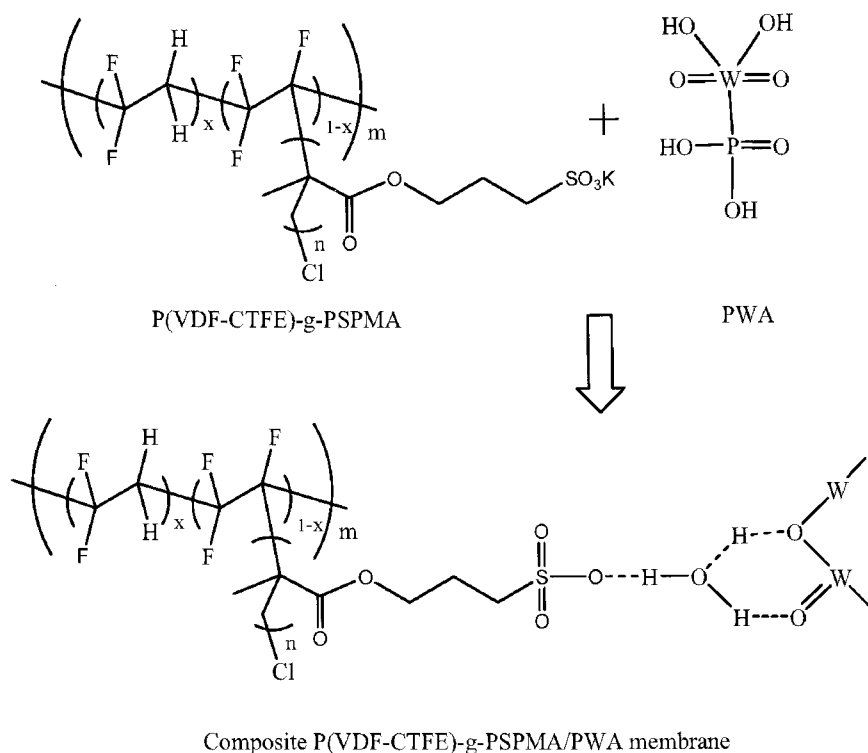
**Scheme 2.** Schematic procedure for P(VDF-CTFE)-g-PSPMA/HPA composite membranes.
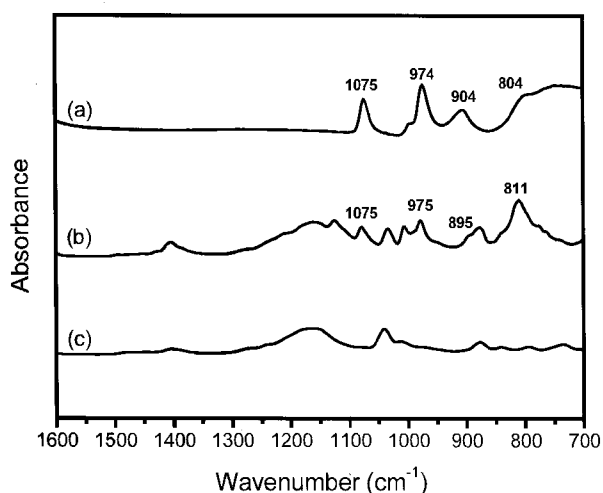
Fig. 2. FT-IR spectra of (a) pure HPA, (b) P(VDF-CTFE)-g-PSPMA/HPA composite membrane and (c) P(VDF-CTFE) graft copolymer.

Upon blending P(VDF-CTFE)-g-PSPMA graft copolymer with HPA, the stretching vibrations of P-O and W=O$_t$ were hardly changed. It demonstrates that these groups do not actively participate in the interaction of the composite polymer electrolyte membranes. On the other hand, stretching vibrations of W-O$_c$-W and W-O$_c$-W significantly shifted to 895 and 811 cm^{-1}, respectively, representing that the hydrogen bonding interactions occurs between the bridging oxygens in the HPA molecules with the sulfonic acid (SO$_3$H) in the PSPMA domains. Favorable interactions of bridging oxygens compared to terminal oxygens might be related to their greater basicity. These IR results show the successful incorporation of the HPA nanoparticles into the P(VDF-CTFE)-g-PSPMA graft copolymer matrix.
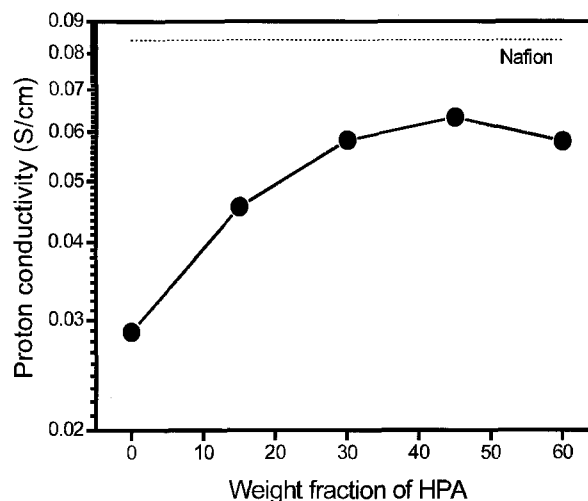
The water uptake of membranes plays an important role in determining the proton conductivity and the mechanical properties of membranes. Thus the water uptake of composite polymer electrolyte membranes was measured by varying the concentrations of HPA as shown in Fig. 3. The pristine P(VDF-CTFE)-g-PSPMA graft membrane exhibited 105% of water uptake. Upon blending the P(VDF-CTFE)-g-PSPMA graft copolymer with HPA, the water uptake of the
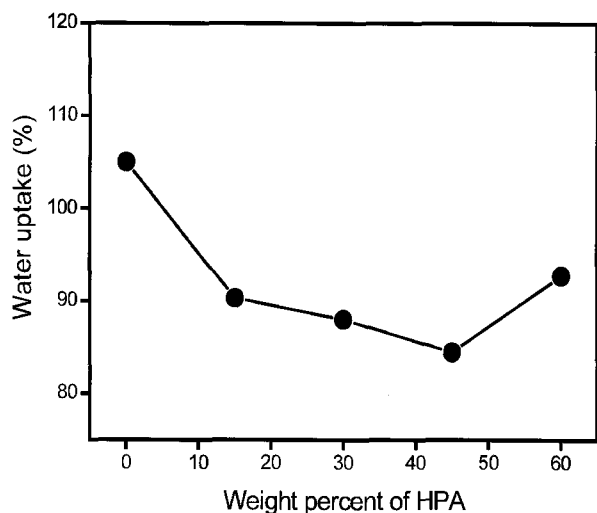
Fig. 3. Water uptake of P(VDF-CTFE)-g-PSPMA/HPA composite membranes with various concentrations.

Fig. 4. Proton conductivity of P(VDF-CTFE)-g-PSPMA/HPA composite membranes with various concentrations.

composite membranes continuously decreased with the increase of HPA content up to 45 wt%, after which it intriguingly increased. The reduced water uptake is attributed to the decrease in number of sulfonic acid as water absorption sites due to the strong hydrogen bonding interaction between the sulfonic acid and the HPA nanoparticles [19-21]. The amount of water molecules absorbed by the composite membranes decreased with an increase in HPA content. Furthermore, the inorganic nanoparticles occupy the micropores in the polymer membranes, which also may contribute towards the reduction in water uptake.

The proton conductivity of P(VDF-CTFE)-g-PSPMA/HPA composite membranes was measured at room temperature using four probe method and compared with that of Nafion 117 in Fig. 4. The pristine P(VDF-CTFE)-g-PSPMA graft copolymer membrane exhibited 0.029 S/cm of conductivity at room temperature. Unique hydrophilic-hydrophobic phase segregated structure between PSPMA and P(VDF-CTFE) would allow the membranes to form clusters with ion-rich channels accounting for proton conduction mechanism. The proton conductivity increased with the increase of HPA contents up to 45 wt%, after which it gradually decreased. The proton conductivity of membrane increases with the increase in water uptake because the forma-

tion of hydrophilic domain is improved with more water uptake. A maximum proton conductivity of 0.063 S/cm was obtained at 45 wt%. The decrease of proton conductivity above 45 wt% is presumably doe to the loss of sulfonic acid groups, resulting from the strong hydrogen bonding interaction between the sulfonic acid and the HPA particles [21].

4. Conclusion

Proton conducting P(VDF-CTFE)-g-PSPMA graft copolymer was synthesized by ATRP using direct initiation of the secondary chlorines of P(VDF-CTFE). This graft copolymer was blended with HPA nanoparticles to form composite polymer electrolyte membranes by varying the HPA and polymer contents. The completion of graft copolymerization and the successful incorporation of HPA were confirmed by FT-IR spectra. The water uptake of the composite membranes decreased from with an increase of HPA contents up to 45 wt% of HPA. The proton conductivity of the composite membranes at room temperature also increased up to 45 wt% HPA, presumably due to both the intrinsic conductivity of the HPA particles and the enhanced acidity of the sulfonic acid of the graft copolymer. Thus a maximum proton conductivity of

the composite polymer electrolyte membranes was achieved as 0.063 S/cm at room temperature at 45 wt% of HPA.

Acknowledgement

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