

PVC-g-PSSA가지형 공중합체와 헤테로폴리산을 이용한 수소이온 전도성 복합 전해질막

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Proton Conducting Composite Membranes Consisting of PVC-g-PSSA Graft Copolymer and Heteropolyacid

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요약: 본 연구에서는 poly(vinyl chloride) (PVC)가지형 공중합체 전해질과 헤테로폴리산(HPA)을 이용하여 유무기 합성 전해질막을 제조하였다. poly(vinyl chloride)-g-poly(styrene sulfonic acid) (PVC-g-PSSA)는 PVC의 이차 염소의 직접적인 개시를 이용한 atom transfer radical polymerization (ATRP)로 합성하였다. 이때, HPA 나노입자는 수소 결합을 통해 PVC-g-PSSA 가지형 공중합체와 결합하는 것을 FT-IR spectroscopy를 통하여 확인하였다. 전해질막의 수소이온 전도도는 HPA의 질량 분율이 0.3이 될 때까지 상온에서 0.049에서 0.068 S/cm로 증가하였다. 이것은 HPA 나노입자 고유의 전도도와 가지형 공중합체가 가지고 있는 술폰산의 강화된 산도 때문이라고 추정된다. 흡습률은 HPA의 질량 분율이 0.45까지 증가할수록 130에서 84%로 감소하였다. 이것은 HPA 나노입자와 고분자 매트릭스 사이의 수소 결합의 상호작용 때문에 물을 흡수하는 site의 수가 감소한 결과라고 볼 수 있다. 열중량 분석결과 HPA의 농도가 증가할수록 전해질막의 열적 안정성이 강화된다는 것을 알 수 있었다.

Abstract: A series of organic-inorganic composite membranes from poly(vinyl chloride) (PVC) graft copolymer electrolyte and heteropolyacid (HPA) were prepared for proton conducting membranes. First, poly(vinyl chloride)-g-poly(styrene sulfonic acid) (PVC-g-PSSA) was synthesized by atom transfer radical polymerization (ATRP) using direct initiation of the secondary chlorines of PVC. HPA nanoparticles were then incorporated into the PVC-g-PSSA graft copolymer through the hydrogen bonding interactions, as confirmed by FT-IR spectroscopy. The proton conductivity of the composite membranes increased from 0.049 to 0.068 S/cm at room temperature with HPA contents up to 0.3 weight fraction of HPA, presumably due to both the intrinsic conductivity of HPA particles and the enhanced acidity of the sulfonic acid of the graft copolymer. The water uptake decreased from 130 to 84% with the increase of HPA contents up to 0.45 of HPA weight fraction, resulting from the decrease in number of water absorption sites due to hydrogen bonding interaction between the HPA particles and the polymer matrix. Thermal gravimetric analysis (TGA) demonstrated the enhancement of thermal stabilities of the composite membranes with increasing concentration of HPA.

Keywords: nanocomposite, heteropolyacid, polymer electrolyte membrane, graft copolymer, proton conductivity

1. Introduction

Polymer electrolytes have received great attention

due to their possible applications as solid electrolytes in electrochemical devices such as lithium rechargeable batteries, dye-sensitized solar cells or facilitated olefin transport membranes [1-5]. Among them, proton conducting polymer electrolytes have been extensively in-

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investigated for the applications to fuel cells during the last decade [6-8]. In polymer electrolyte membrane fuel cells (PEMFC), proton conducting polymer electrolyte membranes are of pivotal importance because they act as a separator to prevent the mixing of reactant gases and also provide ionic pathways for protons transport. The most common polymer electrolyte membranes used in fuel cell applications are perfluorinated polymer membranes, e.g. the Nafion series from DuPont. With a microphase-separated morphology, these membranes exhibit excellent thermal, mechanical and electrochemical properties. However, their commercialization to fuel cells is limited to some degree by some disadvantages such as high cost, high methanol permeability, and loss of membrane performance at evaluated temperature/low humidity conditions. Therefore, an alternative polymer electrolyte membrane should be developed for the success of fuel cell technology [9-13].

An organic-inorganic composite material with nanosize interfaces between organic and inorganic domains offers exceptional opportunities to create novel polymer electrolyte membranes with unique properties [14-18]. For example, the incorporation of inorganic compounds into neat polymer membranes provides enhanced proton conductivity and water retention at high temperatures as well as mechanical strength of membranes. Heteropolyacid (HPA) is one of the most attractive inorganic modifiers for proton exchange membranes because of their higher conductivity and thermal stability in crystalline form.

In this study, we synthesized poly(vinyl chloride)-*g*-poly(styrene sulfonic acid) (PVC-*g*-PSSA) by atom transfer radical polymerization (ATRP) using direct initiation of the secondary chlorines of PVC and then blended with HPA at various weight ratios. The hybrid organic/inorganic nanocomposite membranes were characterized in terms of proton conductivity, water uptake and thermal properties. A particular attention is also focused on the specific hydrogen bonding interactions between the PVC-*g*-PSSA graft copolymer and the HPA particles to provide insight into the molecular

structure of the nanocomposite membranes.

2. Experimental

2.1. Materials

Poly(vinyl chloride), 4-styrenesulfonic acid sodium salt hydrate (SSA), 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 PVC-*g*-PSSA Copolymer

In a 50 mL vial, 14 g of SSA was dissolved in 54 mL of DMSO at 70°C. In 250 mL round bottom flask, 2 g of PVC was dissolved in 28 mL of NMP at 70°C. The SSA solution was added to the PVC 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 hour. 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. PVC-*g*-PSSA copolymer was obtained and dried in a vacuum oven overnight at room temperature.

2.3. Preparation of Composite Polymer Electrolyte Membranes

The composite membranes containing HPA in various weight ratios were prepared using a solution casting method. First, the as-synthesized PVC-*g*-PSSA 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

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

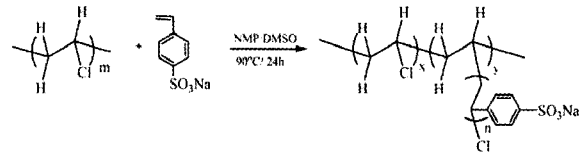
where W_w and W_d are the weights of wet and dried membranes, respectively.

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 1~8 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 [13,19].

2.6. Characterization

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. The thermal properties of the copolymer membranes were determined by thermal gravimetric analysis (TGA, Mettler Toledo TGA/SDTA 851e, Columbus, OH). TGA measurements were performed



Scheme 1. Synthetic procedure for PVC-g-PSSA graft copolymer via ATRP.

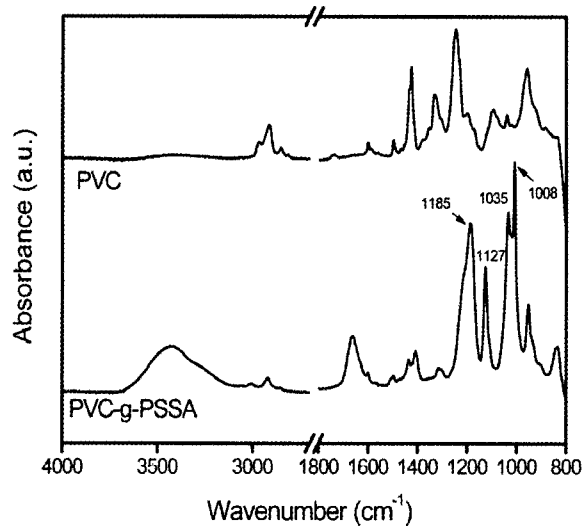


Fig. 1. FT-IR spectra of pristine PVC and PVC-g-PSSA graft copolymer.

from room temperature to 600°C at a rate of 20°C/min. The amounts of the membranes were determined as a weight loss percentage during heating.

3. Results and Discussion

3.1. Synthesis of PVC-g-PSSA Electrolyte

The schematic diagram illustrating the synthesis of PVC-g-PSSA copolymer electrolyte is presented in Scheme 1. PVC backbone was directly grafted with styrene sulfonic acid (SSA) at 90°C for 24 h through ATRP technique. The amphiphilic PVC graft copolymer is expected to molecularly self-assemble into continuous nanophase domains of semicrystalline PVC interweaved with hydrophilic proton conducting domains of PSSA brush layer, providing a mechanism for facile proton transport through the membranes [20,21]. The graft copolymer has a composition of 56:44 wt% in PVC:PSSA, according to the ^1H NMR analysis.

Fig. 1 presents the FT-IR spectra of PVC and PVC-

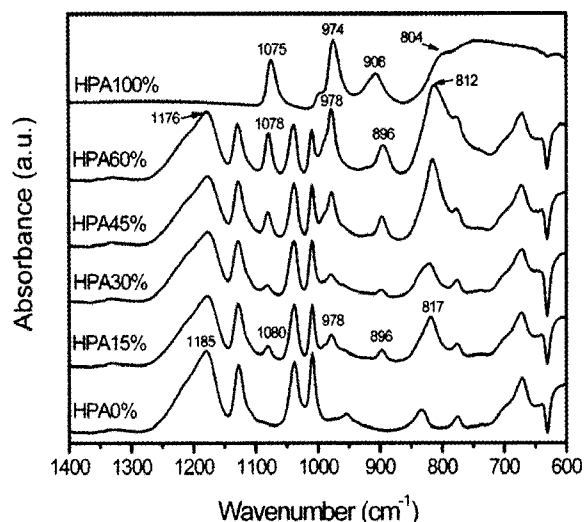
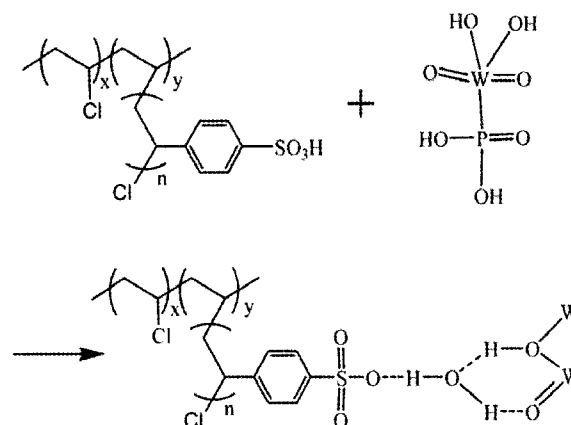


Fig. 2. FT-IR spectra of the composite polymer electrolyte membranes comprising PVC-g-PSSA and HPA with various concentrations.

g-PSSA copolymer synthesized by ATRP. Compared to the pristine PVC, the PVC-g-PSSA graft copolymer exhibited the strong absorption bands at 1,185, 1,127, 1,035, 1,008 cm^{-1} . These bands result from the stretching vibrations of phenyl rings substituted with sulfonate groups and sulfonate anions attached to phenyl ring [22]. The broad absorption band at around 3,435 cm^{-1} is attributed to the 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 PVC backbone.

3.2. Preparation of Composite Polymer Electrolyte Membranes

The FT-IR spectra of the organic/inorganic composite polymer electrolyte membranes consisting of grafted copolymer (PVC-g-PSSA) and HPA with various weight ratios 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 (HPA 100%), 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) [15]. When the PVC-g-PSSA graft copolymer was combined with HPA, the stretching vibrations of



Scheme 2. Schematic structure for composite electrolyte membranes of PVC-g-PSSA graftcopolymer and HPA.

P-O and W = O_t slightly changed to 1,078 ($\Delta f = 3 \text{ cm}^{-1}$) and 978 cm^{-1} ($\Delta f = 4 \text{ cm}^{-1}$), respectively. 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_e-W significantly shifted to 896 ($\Delta f = 12 \text{ cm}^{-1}$) and 817 cm^{-1} ($\Delta f = 13 \text{ cm}^{-1}$), respectively. These results represent that the hydrogen bonding interactions take place between the bridging oxygens in the HPA molecules with the sulfonic acid (SO₃H) in the PSSA domains. Favorable interactions of bridging oxygens compared to terminal oxygens might be related to their greater basicity. These absorptions prove the successful incorporation of the HPA nanoparticles into the PVC-g-PSSA graft copolymer matrix. The resulting schematic structure of the graft copolymer and HPA composite polymer electrolyte membranes is illustrated in Scheme 2.

3.3. Water Uptake

The water uptake of membranes plays an important role in determining the proton conductivity and the mechanical properties of membranes. It is because the proton exchanging reaction requires a significant amount of water to coordinate with proton as it moves through the membranes [23]. Thus the water uptake of composite polymer electrolyte membranes was evaluated by varying the concentrations of HPA as shown in Fig. 3. The pristine PVC-g-PSSA graft membrane exhibited

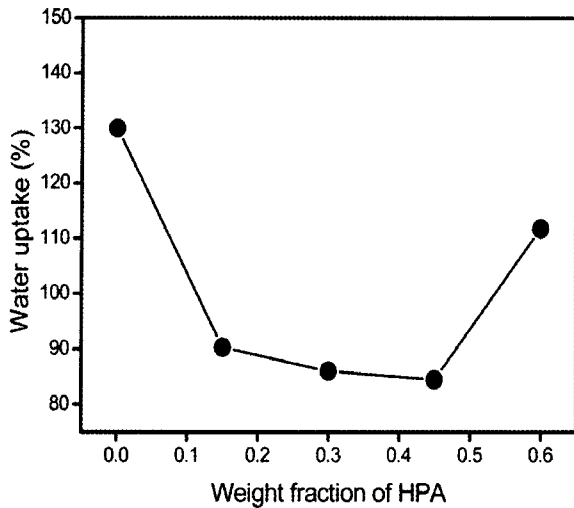


Fig. 3. Water uptake of composite polymer electrolyte membranes comprising PVC-g-PSSA and HPA with various concentrations.

130% of water uptake, which is roughly three times higher than that of Nafion. Upon blending the PVC-g-PSSA graft copolymer with HPA, the water uptake of the composite membranes continuously decreased with the increase of HPA content up to 0.45 of weight fraction of HPA, after which it intriguingly increased. The minimum water uptake of 84% was observed at 0.45 of weight fraction of HPA. 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 [14,15]. As illustrated in Scheme 2, the HPA molecules preferentially interact with sulfonic acid groups, resulting in the decreased number of free sulfonic acid groups available to form hydrogen bond with water molecules. Consequently, 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.

3.4. Proton Conductivity

The fuel cell performances strongly dependent on the proton conductivity of polymer electrolyte membranes,

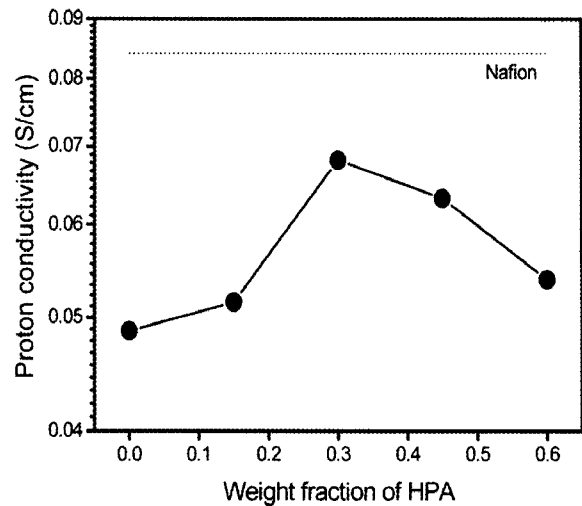


Fig. 4. Proton conductivity of composite polymer electrolyte membranes comprising PVC-g-PSSA and HPA with various concentrations.

and thus the proton conductivity would be of pivotal importance in fuel cell membranes. The proton conductivity of PVC-g-PSSA/HPA composite membranes was measured at room temperature using four probe method and compared with that of Nafion 117 in Fig. 4. The pristine PVC-g-PSSA graft copolymer membrane exhibited 0.049 S/cm of conductivity at room temperature. Unique hydrophilic-hydrophobic phase segregated structure between PSSA and PVC would allow the membranes to form clusters with ion-rich channels accounting for proton conduction mechanism [24]. The proton conductivity increased with the increase of HPA contents up to 0.3 of HPA weight fraction, after which it gradually decreased. Generally, the proton conductivity of membrane increases with the increase in water uptake because the formation of hydrophilic domain is improved with more water uptake. In this work, however, the proton conductivity increased with increasing HPA amounts up to 0.3 of HPA weight fraction even though the water uptake decreased. This result is presumably due to both the intrinsic conductivity of HPA nanoparticles and the enhanced acidity of the sulfonic acid of the polymer matrix by HPA incorporation [14,15]. Therefore, a maximum proton conductivity of 0.068 S/cm was achieved at 0.3 of HPA weight fraction. The continuous decrease of pro-

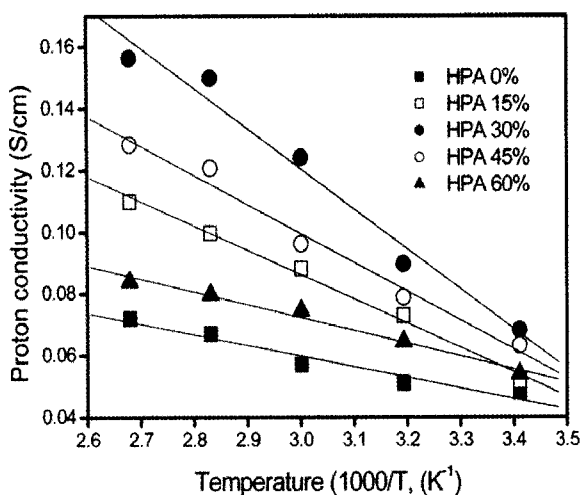


Fig. 5. Temperature dependence of proton conductivities for PVC-g-PSSA/HPA composite membranes.

ton conductivity above 0.3 is considered to result from the loss of ionic sites, i.e. sulfonic acid (SO_3^-), which is presumably due to the strong hydrogen bonding interaction between the sulfonic acid and the HPA particles [25].

The proton conductivities of the PVC-g-PSSA/HPA composite membranes were also measured as a function of temperature and provided in Fig. 5. As expected, the proton conductivities increased with the increase of temperature for all the membranes. This temperature dependent conductivity can be explained by the fact that the increase of temperature favors both the dynamics of proton mobility and the structural re-orientation of polymeric chains, resulting in the increased proton conductivity at high temperatures [26]. The increase of proton conductivity in PVC-g-PSSA/HPA composite membranes with the increase in temperature is more significant for the membranes containing higher HPA concentrations, as revealed by the slopes of the conductivity curves. This is presumably related to the capability of the composite membranes to withhold water strongly even at high temperatures due to the caging effect and hydrogen bonding between the sulfonic acid and the HPA particles. Hence most of the HPA were retained in the polymer and this increases the efficiency of the membrane. Generally proton transfer is facilitated in the presence

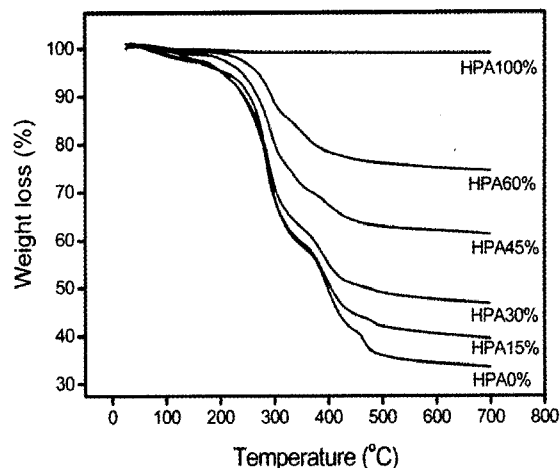


Fig. 6. TGA data of pure HPA, PVC-g-PSSA and PVC-g-PSSA/HPA composite membranes with various concentrations.

of water molecules. Since the amount of water molecules trapped in the polymer increases with HPA content, the conductivity increased with increase in HPA content at the elevated temperature.

3.5. Thermal Properties

The thermograms were recorded under nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. The TGA data of pure HPA, pristine PVC-g-PSSA, and the PVC-g-PSSA/HPA composite membranes with different weight ratios are shown in Fig. 6. The TGA curve for the pure HPA exhibited a slight weight loss at around 120°C due to dehydration, and then no further significant weight loss was observed until 600°C . The PVC-g-PSSA/HPA composite membranes exhibited a three-step thermal degradation pattern. The first weight loss was found around 100°C which is due to the loss of moisture which is absorbed by the highly hygroscopic composite membranes. The second step of degradation at around 250°C corresponds to the degradation of the sulfonic acid groups. The third step at around 400°C indicates the decomposition of the main-chain backbone. Upon blending PVC-g-PSSA with HPA, the second weight loss at around 250°C became less noticeable, resulting from the hydrogen bonding interaction between the sulfonic acid groups and the HPA particles. These TGA data represent that the ther-

mal stability increases with increasing HPA contents and the PVC-g-PSSA/HPA composite membranes exhibited good thermal stability up to around 250°C. The high residual weight of the composite membranes with HPA is considered to be due to the increased amounts of inorganic material which does not undergo decomposition up to 700°C.

4. Conclusion

Proton conducting PVC-g-PSSA graft copolymer at 56:44 wt% was synthesized by ATRP using direct initiation of the secondary chlorines of PVC. 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 proton conductivity of the composite membranes increased from 0.049 to 0.068 S/cm at room temperature up to 0.3 weight fraction of 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 0.068 S/cm at room temperature at 0.3 of HPA weight fraction. The water uptake of the composite membranes decreased from 130 to 84% with an increase of HPA contents up to 0.45 of weight fraction of HPA, resulting from the decrease in number of water absorption sites due to hydrogen bonding interaction between the HPA particles and the graft copolymer matrix. The composite polymer electrolyte membranes were quite stable up to 250°C, which is attributable to the strong specific interaction of the HPA particles with the sulfonic acid of polymer matrix.

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