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Intensively Enhanced Conductivity of Polyelectrolytes by Amphiphilic Compound Doping

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Abstract: As pyrenesulfonic acid (PSA) is added to sulfonated poly(styrene-b-isoprene-b-styrene) (s-SIS), a novel effect on the conductivity of polyelectrolytes results. In this study, s-SIS was sulfonated to two different degrees to obtain s-SISL (ion-exchange capacity (IEC):0.92) and s-SISH (IEC:1.20). After PSA was added to the s-SISL, proton conductivity increased significantly and reached an optimum at a PSA addition of 4% (s-SISL4.0), where the conductivity (0.6×10^{-2} Scm^{-1}) was 6.0 times higher than s-SISL without PSA (0.1×10^{-2} Scm^{-1}). Similarly, when PSA was added to s-SISH (IEC:1.20), the proton conductivity achieved an optimum at a PSA addition of 2% (s-SISH2.0), at which point the proton conductivity (5.3×10^{-2} Scm^{-1}) was 26 times that of s-SISH without PSA (0.2×10^{-2} Scm^{-1}). From the TEM analyses of the s-SISH membrane in the presence of different PSA concentrations, this doping PSA effect can be interpreted by means of the interaction between the aromatic ring on the PSA and the aromatic ring on the hydrophobic polystyrene segments of s-SIS block copolymer. This effect of doping an amphiphilic compound to polyelectrolytes to intensify the conductivity can be widely applied to numerous kinds of polyelectrolytes.

Keywords: pyrenesulfonic acid, polyelectrolyte, ionic cluster, sulfonated poly(styrene-b-isoprene-b-styrene), amphiphilic compound

1. Introduction

Fuel cells are a clean and efficient electrochemical power source that generate electric power via a chemical reaction of fuels.[1] Further, fuel cells have recently received tremendous attention because of their potential to achieve higher efficiencies with renewable fuels at a lower environmental cost than current power sources.[2]

Polyelectrolyte is a key material in many kinds of electronic devices, e.g. fuel cells, capacitors and lithium batteries. For fuel cell application, proton conductivity of polyelectrolyte is a very important factor influencing performance and transport properties, which in turn are dependent on polymer morphology or ionic nanostructure.[3-5] A number of investigations have shown that increasing ion content in proton exchange membranes (PEM) results in an increase in proton conductivity, water content, and methanol crossover.[6-8] Also, it is evident that the diffusion of protons, water, and methanol is affected by the ionic nanostructure and follows a percolation model.[9-14]

Nafion[15-20] is an commercial polyelectrolyte for PEM, alternative[21-27] copolymers have been developed, including polysulfones, polyimides, poly(benzimidazole), and styrene copolymers, which have an -SO_3H group to conduct protons. When fabricated into a membrane, the above alternatives inherently contain a high level of hydrophobic moiety, which reduces water content and decreases conductivity.

In this study, we used a simple amphiphilic compound, pyrenesulfonic acid (PSA), that interacts with the hydrophobic moiety of a copolymer (sulfonated poly(styrene-*b*-isoprene-*b*-styrene), s-SIS) and simultaneously provides –SO_3H hydrophiles to the ionic clusters, which enables the water pool to continue and become more homogeneous, as shown in scheme 1. After doping the sulfonated poly(styrene-b-isoprene-b-styrene) (s-SISH, ion-exchange capacity (IEC): 1.20) membranes with 2% PSA, its very low conductivity was enhanced 26 times from 1.0×10^{-3} S cm^{-1} to 5.3×10^{-2} S cm^{-1}, which is twice the proton conductivity of Nafion-117 (2.6×10^{-2} S cm^{-1}).

2. Experimental Section

2.1 Materials

Styrene (99%) was purchased from ACROS, and isoprene (99%) from Alfa, while n-Butyllithium (1.6M) was procured from Chemetall and used as an initiator. Cyclohexane (100%) was obtained from TEDIA and the methyl alcohol anhydrous (100%) from Mallinckrodt. The ethanol (95%) used in this study was bought from Uniward and the p-Dioxane (99.9%) from J.T Baker. Fuming sulfuric acid (20% SO_3) and pyrenesulfonic acid hydrate (95%) were obtained from Sigma-Aldrich with the tetrahydrofuran (THF) supplied from FULLIN.

2.2 Synthesis of Poly(styrene-b-isoprene-b-styrene) (SIS)

SIS triblock copolymers were prepared by living anionic polymerization in the sequential order of styrene, n-butyllithium, isoprene, and styrene as a reference. [28]

2.3 Sulfonation of SIS Triblock Copolymer (s-SIS)

The sulfonation procedure used in this study was conducted as follows: a 5 wt% solution of SIS in p-dioxane was prepared under a nitrogen atmosphere. A p-dioxane/ sulfur trioxide complex was added to the SIS solution at room temperature and stirred for 2 hr, following a procedure reported in the literature[29]. After sulfonation was complete, the reaction was terminated by slowly adding deionized (DI) water to obtain sulfonated poly(styrene-b-isoprene-b-styrene) with a higher ion-exchange capacity (IEC) value:1.20 and lower IEC value (IEC:0.92), which was donated as s-SISH and s-SISL, respectively. Then, the membrane was isolated by evaporating organic solvents under reduced pressure, and subsequently washed several times with DI water until a pH of 7 was achieved. Finally, the obtained s-SIS was cut into pieces and dried in a vacuum oven at room temperature.

2.4 Preparation of membrane of s-SIS containing PSA

s-SISH and PSA were separately dissolved in THF under vigorous agitation. Subsequently, solutions with different amounts of PSA (content (α) = [Pyrenesulfonic acid]/{[Pyrenesulfonic acid] + [s- SISH]}; α= 0%, 0.5%, 1.0%, 1.5%, 2.0%, 2.5% and 3.0% for membranes of s-SISH, s-SISH0.5, s-SISH1.0, s-SISH1.5, s-SISH2.0, s-SISH2.5, and s-SISH3.0, respectively) were slowly mixed into the s-SISH solution, the resulting solution of which was mixed thoroughly. Further, PSA was slowly added to s-SISL (content (α) = [Pyrenesulfonic acid]/{[Pyrenesulfonic acid] + [s-SISL]}; α= 0%, 1.0%, 2.0%, 3.0%, 4.0%, and 5.0% for membranes of s-SISL, s-SISH1.0, s-SISH2.0, s-SISH3.0, s-SISH4.0, and s-SISH5.0 respectively) and was also thoroughly mixed. Then, the mixture were poured onto a Teflon plate, followed by slow evaporation of the residual solvent at 30 °C for 12 hr. Finally, the hybrid copolymers were washed several times with DI water until a pH of 7 was achieved.

2.5 Characterizations

All NMR experiments were performed on a Bruker Avance-500 spectrometer at a proton resonance frequency of 500.13 MHz. The proton chemical shifts were referenced to the tetramethylsilane (TMS) signal at 0.0 ppm and $CHCl_3$ signal at 7.26 ppm.

The molecular weight measures were determined by Gel Permeation Chromatography (GPC) with a Waters 410 differential refractometer and calibrated with polystyrene (PS) linear standards. Tetrahydrofuran was used as the carrier at 1 mL min^{-1} under a high-pressure liquid chromatographic gradient.

Thermogravimetric analysis (TGA) measurements were conducted on a PerkineElmer TGA-7 under a dry nitrogen atmosphere over the temperature range of 120-600 ℃ at a heating rate of 20 ℃ min^{-1}.

The ion exchange capacity (IEC) was measured by classic titration.[30] The membranes were soaked in a saturated NaCl solution (20 ml 2.0 M NaCl solution) with released protons titrated using a 0.05 N NaOH aqueous solution.

Differential scanning calorimetry (DSC) measurement for fully-hydrated membranes was conducted on a DuPont TA2010 analyzer at a heating rate of 5 °C min^{-1} from -50 °C to 30 °C under a dry nitrogen atmosphere, and with an empty aluminum pan as a reference to obtain freezing water (ω_f). [31-32] The weight fraction of bound water (ω_b) was calculated by subtracting the amount of freezing water from the total water content (ω_t).

The polymer membranes' proton conductivity was measured by an AC impedance technique using an electrochemical impedance analyzer (CH Instrument model 604A), for which the AC frequency was scanned from 100 kHz to 10 Hz at a voltage amplitude of 10 mV. Fully hydrated membranes were sandwiched into a Teflon conductivity cell fitted with gold plates. Temperature dependence of the proton conductivity was performed by controlling the temperature from 30 to 80 ℃ at a relative humidity of 95 %.

The cross-section morphology of the membranes was characterized by transmission electron microscopy (TEM) using a JEOL JEM-1200CX-II microscope operating at 120 kV. To promote hydrogen ion exchange, the hybrid membranes were immersed in 0.1 N Ag^+ aqueous solution for two days, and then rinsed with DI water to remove the residual solution. A 3 x 5 mm strip was cut from the membranes and dried under vacuum at 80 ℃ for 12 hr, after which the sample was sectioned into 50 nm slices using an ultramicrotome, and placed onto 300-mesh copper grids for TEM observation.

3. Results and Discussion

3.1 Preparation and characterization of SIS copolymers, sulfonated copolymers (s-SIS) and their blendings with PSA

Copolymer SIS was prepared via anionic polymerization and characterized by ^{1}H NMR and GPC. As shown in Figure 1, the peaks at 7.3–6.3 ppm are due to the benzene rings' proton in the PS block, while the two characteristic peaks at 5.1 and 4.8 ppm are induced by the polyisoprene (PI) proton adjacent to the double bonds of the 1,4-PI and 3,4-PI units, respectively.[33] From the ^{1}H NMR spectra of the copolymer with increasing sulfonation levels, a gradual disappearance of the signals at 5.2 and 4.7 ppm and a gradual appearance of a new signal at 3.7 ppm were observed, indicating the occurrence of the sulfonated reaction. After sulfonation, the peaks corresponding to the protons on the benzene ring at 7.3-6.3 ppm were unchanged. This demonstrates that sulfonation occurred only through the isoprene block of SIS without any sulfonation on the PS block.

Several composite were obtained by mixing different weight ratios (α) of PSA (α = 0.0-5.0%) with the copolymers, for which the ion exchange capacities (IECs) were titrated to be ranging from 0.92 to 1.26 mequiv. g^{-1}, as shown in Table 1.

3.2 Thermal stability of SIS/ s-SISH

The thermal stabilities of unsulfonated, sulfonated and blended copolymers were evaluated by TGA curves, as shown in Figure 2. For SIS, the degradation at 360 ^{o}C was due to decomposition of the polymer skeleton. In addition, s-SISH showed two weight loss stages associated with two degradation temperatures at 150 and 450 ^{o}C, which is the same result as the with reference[34]. It can therefore be concluded that the sulfonation of SIS enhances the thermal stability of the polymer (s-SISH) by increasing its degradation temperature.[35]

3.3 Proton conductivity enhanced by doping PSA

The value of IEC and *in-plane* proton conductivity (σ) of the hybrid membranes at the constant relative humidity (R.H.) of 95% is summarized in Table 1. As shown, an s-SISL copolymer with an IEC value (0.92) similar to that of Nafion-117 was synthesized, the s-SISL membrane of which has a lower proton conductivity (0.1×10^{-2} Scm^{-1}, 30 °C) than Nafion-117 (2.6×10^{-2} Scm^{-1}, 30 °C). As PSA was gradually added into the s-SISL up to 5%, it was observed that the proton conductivity kept increasing; be that as it may, there exists an optimum addtion amount at 4% where the conductivity is 6.0 times higher than that of the s-SISL membrane without PSA (as shown in Table 1). In order to increase proton conductivity, we synthetized s-SISH with a higher IEC value to obtain more $–SO_3H$ groups in the hydrophilic part (IEC value:1.20).

The proton conductivity of s-SISH with an IEC value of 1.20 is 0.2×10^{-2} Scm^{-1}, which although is higher than that of s-SISL with an IEC of 0.92 (0.1×10^{-2} Scm^{-1}, 30℃, Table1), is still much lower than that of Nafion-117 (2.6×10^{-2} Scm^{-1}, 30 °C). As PSA was gradually added to s-SISH (IEC:1.20), the proton conductivity significantly increased and reached a maximum when the added PSA was 2% (Figure 3), at which point the proton conductivity was 5.3×10^{-2} (30 °C). It is very interesting to note that an addition of only 2% PSA into s-SISH (IEC:1.20), donated as s-SISH2.0, could increase the conductivity of s-SISH 26-fold as compared to s-SISH without PSA (0.2×10^{-2}, 30 °C). Moreover, the proton conductivity of s-SISH2.0 is twice that of Nafion-117 (2.6×10^{-2}, 30 °C).

In general, the proton conductivity of s-SISH*x* membranes increases with an increasing upon the PSA content, but s-SISH2.5 and s-SISH3.0 show lower conductivities (2.3×10^{-2} Scm^{-1} and 1.8×10^{-2} Scm^{-1}, 30 ℃, respectively). More specifically, a Λ-shaped curve of proton conductivities is found for s-SISH*x* membranes as a function of PSA wt %, as shown in Figure 3. This Λ-shaped curve is likely due to the larger water sorption of s-SISH2.5 and s-SISH3.0 inducing higher deformation and lower ionic density in the swollen membranes. Figure 4 shows that the dependence of proton conductivity on temperature follows an

Arrhenius relationship for all membranes, the slopes of which are all similar for each PSA/copolymer suggesting that these membranes had the same proton transfer kinetics involving Grotthus-type conduction and had a lower proton transfer kinetics than s-SISH (high activation energy).

3.4 Water content and states of water

To better understanding the intensively enhanced conductivity of s-SISH via doping with PSA, the total water content (ω_t), bound water (ω_b), and freezing water (ω_f) of s-SISH influenced by different PSA-dosages were measured and calculated.

Generally, it is believed that protons can be transported along with cationic mixtures such as H_3O^+ and H_5O^{2+} in aqueous medium.[36]An appropriate water content level must be maintained in sulfonated polymer membranes to obtain high $-SO_3H$ density and ensure good proton conductivity. After immersion in water, the water content of the s-SISH*x* composite membranes (at 30 ℃) with various PSA concentrations were measured and compared, as shown in Table 2. An increase in the PSA ratio led to an increase in water content (ω_t, grams of water adsorbed per gram of hydrated membrane) and IEC value. Furthermore, the association of water molecules with species such as ionic and polar groups dominates the thermal transitions of the water molecules.[37] Consequently, bound water that forms a true solution with the polymer does not freeze at 0 °C.[38] The DSC thermograms of the fully hydrated s-SISH*x* membranes in Figure 5 show that all samples had an endothermic peak at around -2.0 to 0.0 °C. The number of total water molecules per sulfonic acid group, λ_t, was calculated by

$$\lambda_t = \frac{\omega_t}{18 \cdot \mathrm{IEC} \cdot (1-\omega_t)}$$

where ω_t is the total water content (free λ_f was calculated by ω_f while bound λ_b was calculated by ω_b). As shown in Table 2 and Figure 6, for a s-SISH*x* membrane, an increase in PSA wt % from 0.5 to 3% caused an increase in λ_t from 23 meq^{-1} g to 136 meq^{-1} g. This result indicates that the PSA in the s-SISH*x* membrane enhances the association capability of the inherent hydrophilic sites in the blend matrix. Moreover, the number of specific water molecules per sulfonic acid group has been shown to closely correlate with the sizes of ionic clusters in copolymers.[39] Figure 6 displays the dependence of λ_t, λ_f and λ_b on the PSA wt% (α). As can be seen, the increasing concentration of sulfonic acid groups produced an increasing curve with a big jump at PSA 2.5 wt% for $\lambda_{t,}$ but a gradual and slightly increasing curve for λ_f and λ_b. Nevertheless, from the measurements shown in Table 2 and Figure 6, the results of the water content, free water and bound water can not account for the intensive enhancement of the conductivity of s-SISH by doping different levels of PSA. Although increases in IEC and water content of the proton conductive polymer electrolyte led to increases in proton conductivities, larger water sorption may induce larger deformation in the swollen membrane and lower proton conductivity, as was the case for s-SISH2.5 (λ_t:117.5 meq^{-1} g) and s-SISH 3.0 (λ_t:135.9 meq^{-1} g). Therefore, investigation of how the ionic clusters' microenvironment is influenced by PSA through microscopic observations must be performed, as detailed below.

3.5 Microscopic observation of the PSA-doping effects

In order to clearly observe the water content of the polyelectrolyte membrane affected by PSA, the s-SISH membranes, with and without PSA, as well as the comparable Nafion-117 membranes were all dyed with Ag$^+$; than, TEM observations were conducted, the results of which are shown in Figure 7. The dark and light regions represent the localized hydrophilic and hydrophobic domains, respectively. As shown, s-SISL exhibits a larger ionic cluster distance (124.6 nm) than does Nafion-117 (10.9 nm). As PSA 3%, 4%, and 5% was added into s-SISL, it can be observed that the ionic cluster distance decreased, with the optimum addition amount being 4%, i.e. 85.2 nm for s-SISL3.0 (Figure 7a), 19.6 nm for s-SISL4.0 (Figure 7b), and 23.6 nm for s-SISL5.0 (Figure 7c). Moreover, the ionic cluster distance of s-SISL4.0 is 6.4 times lower than that of s-SISL (124.6 nm).

The doping effects of PSA on the polyelectrolytes with higher hydrophilicity (s-SISH) were also observed through TEM, as shown in Figure 7.Although s-SISH features spherical ionic clusters with lower distances (Figure 7a’, 119.2 nm) than s-SISL, the distance between them is too great to be interconnected and constitute a continuous ionic channel. The TEM image of the s-SISH1.5 membrane (Figure 7a’) indicates the existence of a large number of ionic clusters with smaller (11.4 nm) and denser distances (18.2 nm). When the amount of added PSA was increased to 2.0%, (s-SISH2.0, Figure 7b’) it can be clearly observed that the sizes of ionic clusters significantly decreased (5.0 nm) and the cluster distance of become very small (9.5 nm) both of which were smaller than those of Nafion-117 (size: 7.1 nm, distance: 10.9 nm, Figure 7A). The ionic cluster distance of s-SISH2.0 is 12.53 times less than that of the s-SISH membrane and these small and dense ionic clusters very easier form a continuous channel for proton transfer. Conversely, as the dosage of PSA is further increased to 2.5% (s-SISH2.5), the size increased (18.1 nm) and the ion clusters became disconnected (20.6 nm, Figure 7c’). Relationships between the size/distance of ion clusters and conductivity are summarized and compared in Figure 7. It can be concluded that when doping PSA into the s-SISL or s-SISH membrane, It can be concluded that when doping PSA into the s-SISL or s-SISH membrane, the optimum smaller size and ionic distance, which corresponds to higher conductivity, occurs at 4.0 % for s-SISL and 2% for s-SISH. For the optimized s-SISH2.0, as compared with Nafion-117, the size and ionic cluster distance are smaller and the conductivity is double.

The doping effect of PSA on the ionic clusters and conductivity of the s-SISH copolymer were correlated and interpreted through TEM, as shown in Figure 7 and Scheme 1. In this study, the samples of s-SIS and PSA composites for measuring conductivity and TEM were all prepared by dissolving s-SIS/PSA in THF first and then removing the solvent to obtain dry membranes. s-SIS comprises a hydrophilic block of sulfonated-polyisoprene terminated with two hydrophobic blocks of PS, the latter of which is soluble in THF but the former is not.

Therefore, when s-SIS is dissolved in THF, although the PS block becomes extended in solution, the sulfonated-polyisoprene block condenses together to form coagulates. As such, when dyed with Ag^+ the coagulated hydrophilic block of sulfonated-polyisoprene can be clearly observed, but the hydrophobic extended PS block is transparent, shown in Figure 7 and represented in Scheme 1.

If PSA is added to the s-SISH solution, the aromatic ring segment of the PSA interacts with the aromatic ring of PS so as to provide the hydrophobic block of PS with more hydrophilic -SO_3H groups and form bigger coagulates, as shown in Scheme 1. When 1.5 wt% PSA was added into the s-SISH membrane, the number of ionic clusters significantly increased. By contrast, as 2% PSA was added into the s-SISH, the number of PSA coagulates grew and the distributions became more uniform. This phenomenon could be attributed to the increased amount of PSA interacting with the hydrophobic PS block and attracting more hydrophilic ion clusters, which in turn leads to higher conductivity. However as the amount of added PSA increased from 2.0% to 2.5%, the high PSA content forced the PSA-associated hydrophilic block of sulfonated-polyisoprene to aggregate violently, which accounts for the conductivity decreasing from 5.3×10^{-2} to 2.3×10^{-2} Scm^{-1}. In the cases of s-SISH2.5 (λ_t:117.5 meq^{-1} g) and s-SISH 3.0 (λ_t:135.9 meq^{-1} g), the increases in IEC and water content, may also lead to larger water sorption and induce larger deformation in the swollen membranes, resulting in lower proton conductivity and larger ionic distances.

4. Conclusion

s-SIS copolymers were successfully synthesized and characterized by TGA, DSC and TEM. An enhanced PSA-doping effect on the conductivity of polyelectrolytes was found. It was found that the addition of PSA into the s-SISL increased proton conductivity and achieved an optimum at a PSA-doping concentration of 4% (s-SISL4.0), at which point the conductivity (0.6×10^{-2} Scm^{-1}) was 6.0 times (0.1×10^{-2} Scm^{-1}) higher than an s-SISL membrane without of PSA. Similarly, when PSA was added to s-SISH, the proton conductivity reached a maximum with a PSA addition of 2% (s-SISH2.0), where the proton conductivity (5.3x10^{-2} Scm^{-1}) was 26 times higher than s-SISH (0.2x10^{-2} Scm^{-1}). From TEM analysis, the ionic cluster distance of s-SISH2.0 (9.5 nm) was found to be 12.53 times lower than that of s-SISH (119.2 nm). Similarly, the ionic distance of s-SISL4.0 (19.5 nm) was 6.35 times lower than that of s-SISH (124.6 nm), which was the lowest in s-SISL*x* series of membranes. The result of microscopic observation was compared with the trend of conductivity. This PSA-doping effect on conductivity could be interpreted by the interaction between the aromatic rings on the PSA and hydrophobic block of s-SIS block copolymer. Through this interaction, PSA provides the hydrophobic block of s-SIS with hydrophobic -SO_3H groups so as to increase conductivity. Moreover, this conductivity enhancing PSA-doping effect can be applied to many kinds of polyelectrolyte.

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Scheme Captions

Scheme 1 Microscopic observation of s-SISH2.0.

Figure Captions

Figure 1: ^{1}H-NMR spectra of (a) SIS, (b) s-SISL and (c) s-SISH samples.

Figure 2: TGA curves of SIS, s-SISH, s-SISH1.0 and s-SISH2.0 samples under a nitrogen atmosphere.

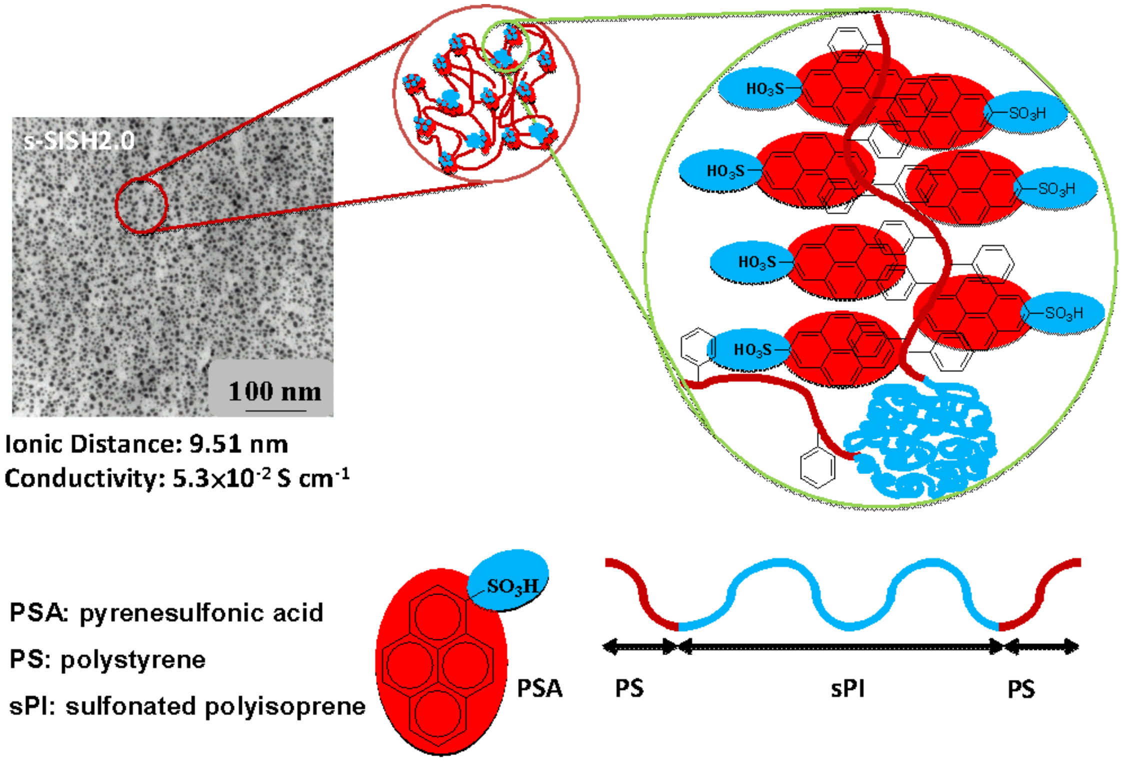
Figure 3: Proton conductivity of hybrid membranes as a function of PSA weight % at 30 ^{o}C.

Figure 4: Arrhenius plots of proton conductivity for Nafion-117 and the hybrid membranes at 95 % RH.

Figure 5: DSC curves of the s-SISH and s-SISH*x*.

Figure 6: Specific water molecules per sulfonic acid group of hybrid membranes as a function of PSA weight %.

Figure 7: TEM micrographs of membranes (A) Nafion-117, (a) s-SISL, (b) s-SISL3.0, (c) s-SISL4.0, and (d) s-SISL5.0; (a') s-SISH, (b') s-SISH1.5, (c') s-SISH2.0, and (d') s-SISH2.5 after dyeing with Ag^+ and the effect of PSA on the conductivity and microscopic observations of polyelectrolyte.



Scheme 1. Microscopic observation of s-SISH2.0.

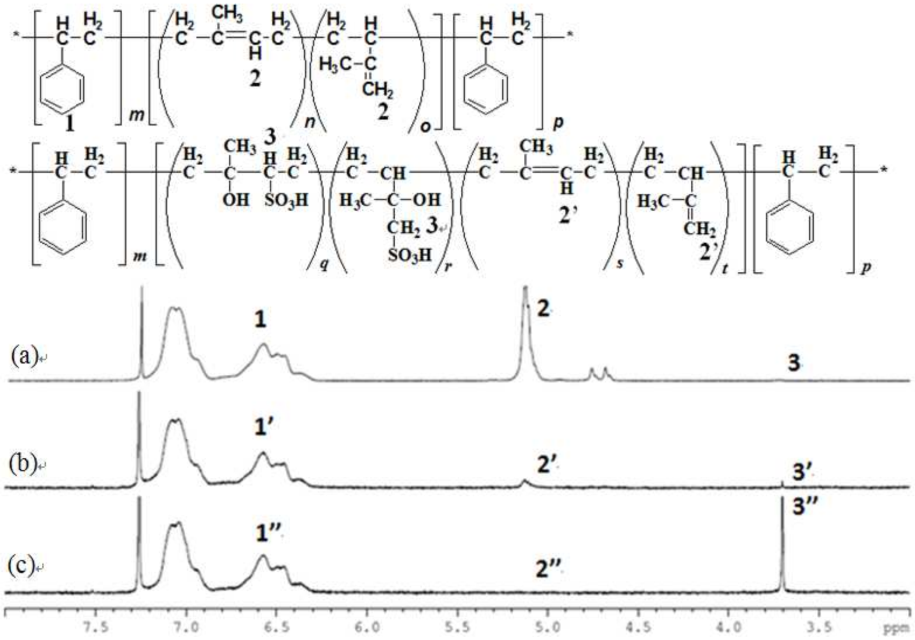


Figure 1. ^{1}H-NMR spectra of (a) SIS ,(b) s-SISL and (c) s-SISH samples.

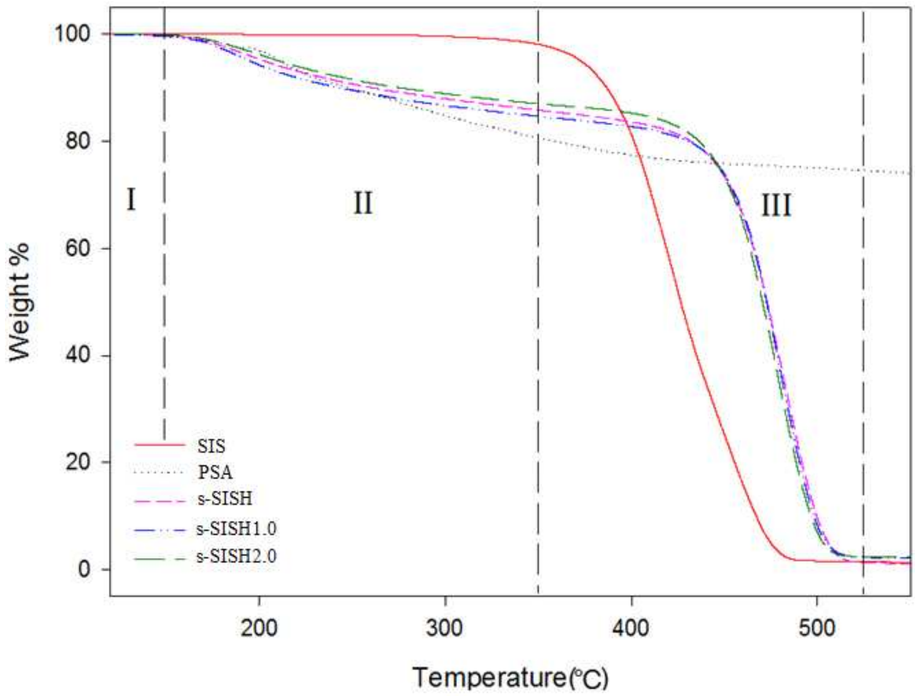


Figure 2: TGA curves of SIS, PSA, s-SISH, s-SISH1.0 and s-SISH2.0 samples under nitrogen atmosphere.

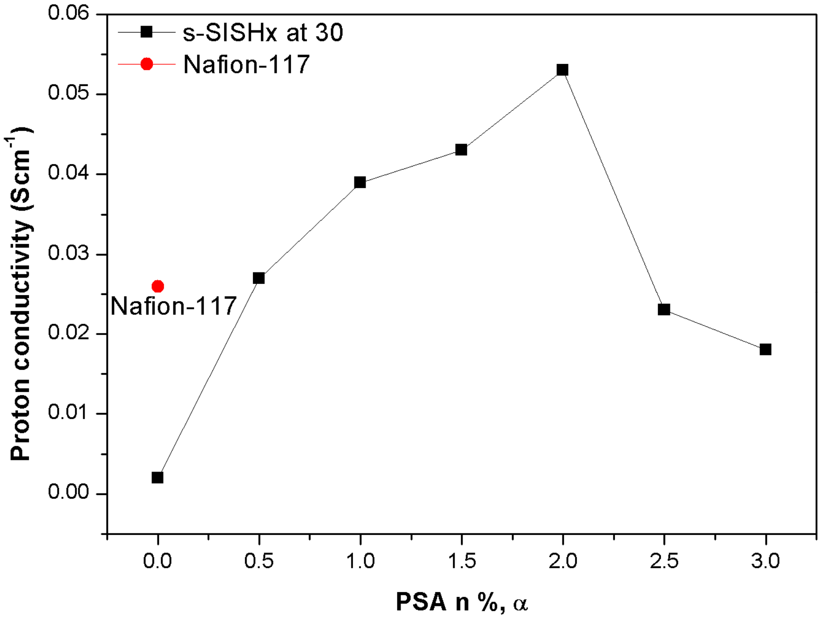


Figure 3: Proton conductivity of hybrid membranes as a function of PSA weight % at 30℃.

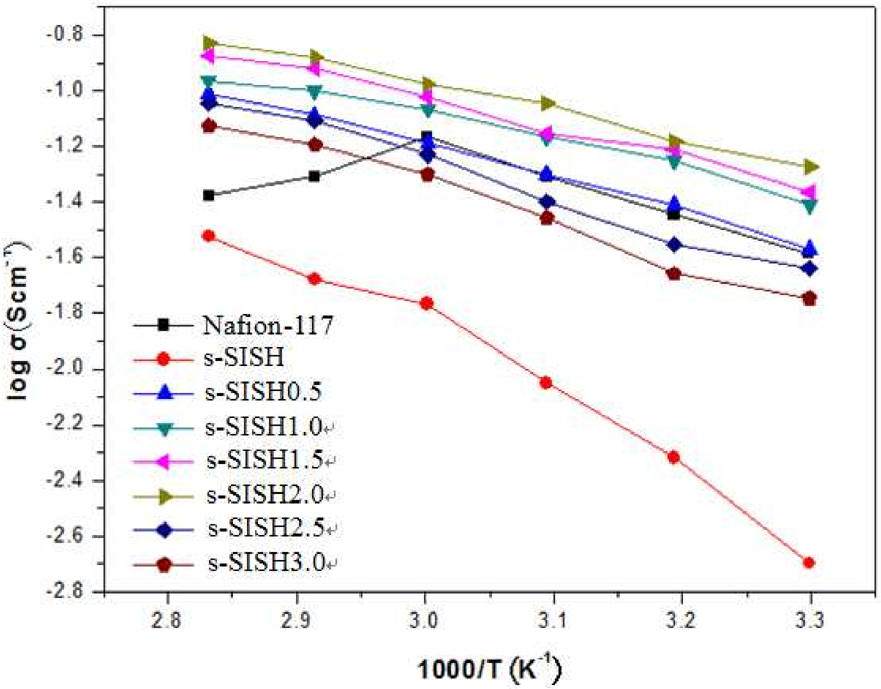


Figure 4: Arrhenius plot of proton conductivity for Nafion-117 and the hybrid membranes at 95 % RH.

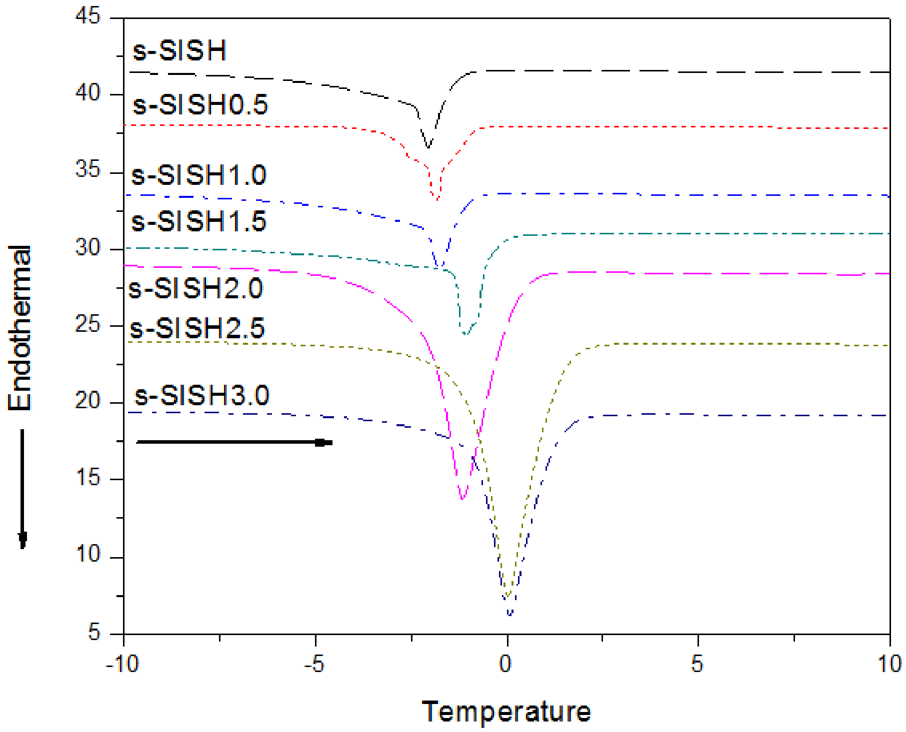


Figure 5: DSC curves of the s-SISH*x*.

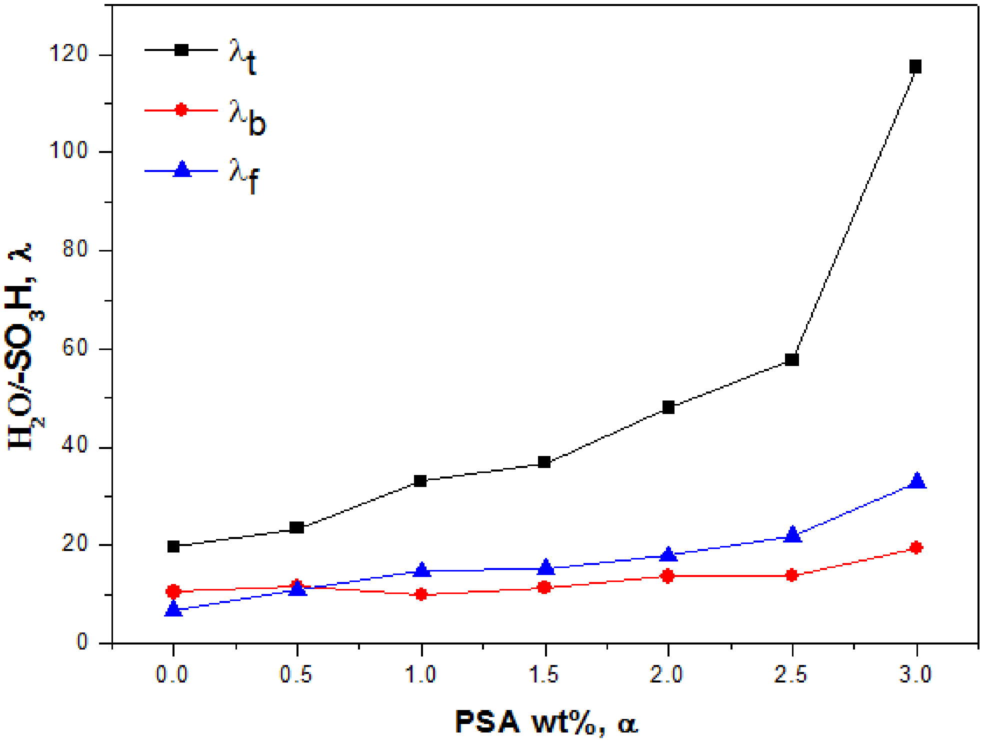


Figure 6: Specific water molecules per sulfonic acid group of hybrid membranes as a function of PSA weight %.

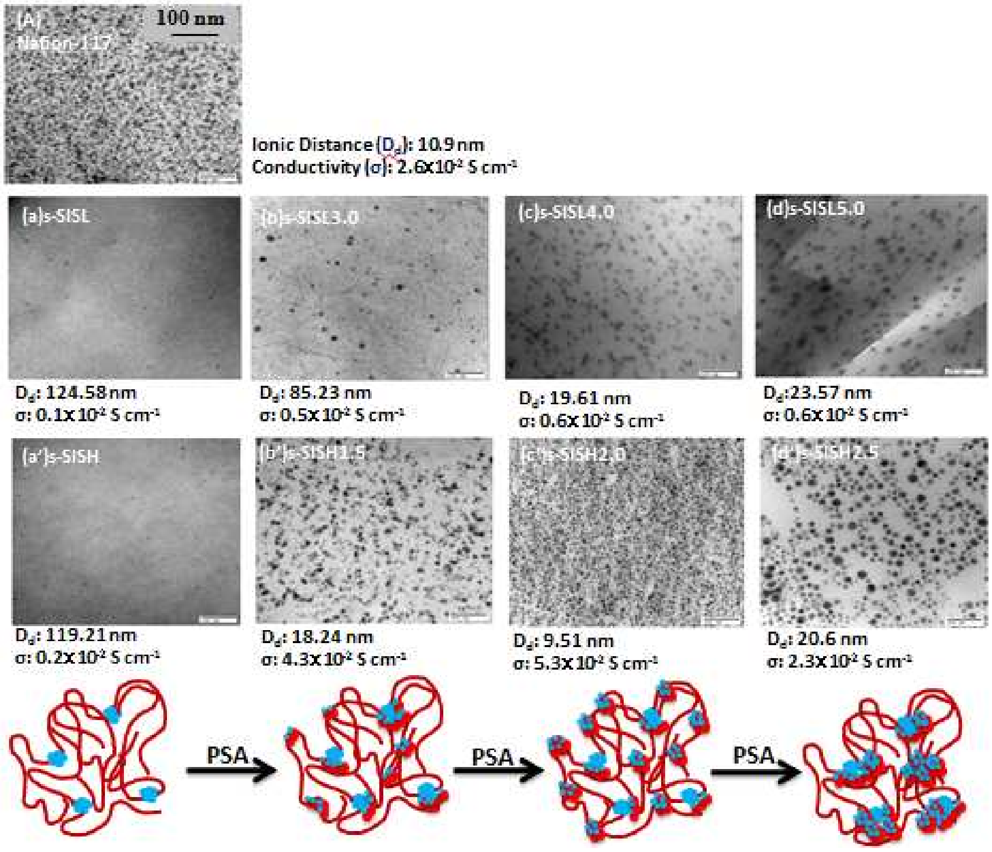


Figure 7: TEM micrographs of (A) Nafion-117 (a) s-SISL3.0 (b) s-SISL4.0 (c) s-SISL5.0 (a') s-SISH1.5 (b') s-SISH2.0 (c') and s-SISH2.5 membranes after stained with Ag^+ and effect of PSA on the conductivity and microscopic observation of polyelectrolyte.

Table 1. The IEC values, proton conductivities and methanol permeabilities of the s-SISL*x* and s-SISH*x* membranes .

Ionomer	**PSA content (α,wt%)**	**IEC (meq g^{-1})**	**Conductivity, ×10^{-2}σ(S cm^{-1})^{a}**			**Ionic Distance (D$_d$) (nm)**
			30^{o}C	**60^{o}C**	**80^{o}C**	
Nafion-117	--	0.91	2.6	6.8	4.2	10.9
s-SISL	0	0.92	0.10	0.1	0.3	124.6
s-SISL0.5	0.5	0.94	0.30	0.8	1.2	-
s-SISL1.0	1.0	0.95	0.31	1.1	1.4	122.5
s-SISL2.0	2.0	0.97	0.32	1.5	2.1	98.2
s-SISL3.0	3.0	1.00	0.51	2.2	3.3	85.2
s-SISL4.0	4.0	1.03	0.61	2.5	4.5	19.6
s-SISL5.0	5.0	1.05	0.60	2.4	4.4	23.6
s-SISH	0	1.20	0.2	1.7	3.0	119.2
s-SISH0.5	0.5	1.21	2.7	6.5	9.8	-
s-SISH1.0	1.0	1.21	3.9	8.6	10.9	33.1
s-SISH1.5	1.5	1.23	4.3	9.5	13.3	18.2
s-SISH2.0	2.0	1.24	5.3	10.6	14.8	9.5
s-SISH2.5	2.5	1.24	2.3	5.9	9.0	20.6
s-SISH3.0	3.0	1.26	1.8	5.0	7.5	-

[a] The proton conductivity at 95 % R.H.

Table 2. The state of water in the s-SISH*x* membranes.

ionomer	water content, ω_t (wt %)[a]	freezing water, ω_f (wt %)	bound water, ω_b (wt %)	bound water degree, χ (%)[b]	λ_t	□λ_b	□λ_f
Nafion-117	24.3	9.8	14.5	59.7	19.6	10.4	6.6
s-SISH	39.0	18.9	20.1	38.9	23.4	11.6	10.8
s-SISH0.5	41.8	24.2	17.6	42.1	33.0	9.8	14.7
s-SISH1.0	44.5	24.9	19.6	44.0	36.8	11.2	15.2
s-SISH1.5	51.5	28.3	23.2	45.0	48.0	13.6	17.8
s-SISH2.0	56.3	32.8	23.5	41.7	57.7	13.8	21.9
s-SISH2.5	72.4	42.2	30.2	41.7	117.5	19.4	32.7
s-SISH3.0	75.5	44.3	31.2	41.3	135.9	20.0	35.1

[a] Measured after immersed in water. [b] $\chi = \omega_b\omega_t^{-1}$.

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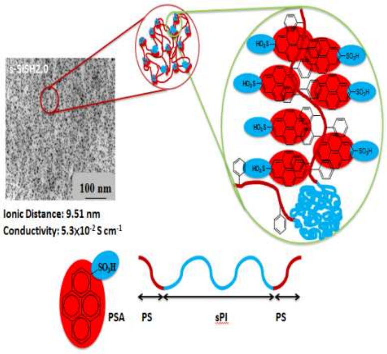
Intensively Enhanced Conductivity of Polyelectrolytes by Amphiphilic Compound Doping

By Huang-Ming Hsu, Chun-Han Hsu and Ping-Lin Kuo*



An simple amphiphilic compound, pyrenesulfonic acid (PSA), which interact with the hydrophobic moiety of a copolymer (sulfonated poly(styrene-*b*-isoprene-*b*-styrene), s-SISH) and simultaneously to provide hydrophiles of -SO$_3$H. As doping 2% PSA to the membranes of s-SISH, enhancing its very low conductivity has been enhanced by 26 times high from 2.0×10^{-3} S cm^{-1} to 5.3×10^{-2} S cm^{-1}.

Keyword: pyrenesulfonic acid, conductivity polyelectrolyte, ionic cluster, sulfonated poly(styrene-b-isoprene-b-styrene), amphiphilic compound