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Synthesis of Sulfonated Polystyrene/acrylate–ionic Liquid (Si-SPS/A–IL) Hybrid Membranes for Methanol Fuel Cells

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Abstract

In this paper, the silicon-containing sulfonated polystyrene/acrylate–ionic liquid (Si-SPS/A–IL) hybrid membranes was prepared to obtain the proton exchange membrane (PEM) materials with high methanol barrier and good selectivity. The Si-SPS/A–IL hybrid membranes characterized as the function of IL to evaluate their potential as PEMs in direct methanol fuel cells (DMFCs).Four different Hybrid material with different properties have been synthesized and named from I to IV.The potential of the membranes in direct methanol fuel cells (DMFCs) is characterized preliminarily by studying their thermal stability, ion-exchange capacity, water uptake, methanol diffusion coefficient, proton conductivity and selectivity (proton conductivity/methanol diffusion coefficient). All the hybrid membranes exhibit good thermal stability and reasonable water uptake. IV and V membranes have a low methanol diffusion coefficient, while II and III membrane have good proton conductivity. In addition, the selectivity values of hybrid membranes increase with increasing IL content and V membrane shows the best selectivity (1.14×10^{5}Ss cm^{-3}). These results suggest that the Si-SPS/A–IL hybrid membranes are possible candidate materials for PEMs in DMFC applications.

Keywords: *Ionic liquid, Direct methanol fuel cell, Hybrid membrane, Proton exchange membrane, Silicon containing membrane.*

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Introduction

Fuel cells because of their particular properties are on the verge of creating a vast revolutionary change in the field of electricity.

Fuels such as H_2, methanol, ethanol, etc. have been usually use in fuel cells [1]. The direct methanol fuel cells (DMFCs) using proton exchange membranes (PEMs) are promising energy conversion devices [2-4]. In DMFCs, the principal function of the PEMs is to allow the transport of protons from the anode to cathode, while prohibiting direct contact of the fuel and the oxidant. Thus, the performance of PEMs is crucial to the functioning of DMFCs [5].To date, perfluorinated polymers such as Nafion® have been perceive as the most suitable PEMs used in PEMFC because of their excellent chemical and physical properties and high proton conductivity. However, the expensive cost, high methanol permeability, loss of conductivity at high temperature (>80˚C) and difficulty in synthesis and processing have limited their wide commercialization [6-7].To improve the performance of PEM, considerable efforts have been devote to modify Nafion® membrane or to develop alternative new non-perfluorinated PEM materials [8–11].

Crosslinking is an effective and simple method to enhance stability and mechanical property of membranes, in particular, to limit the overfull water swelling and methanol diffusion [12–15]. Therefore, for the PEMs used in DMFCs, crosslinking techniques have received extensive attention. In addition, organic/inorganic composites also constitute an emerging research field due to their advantages in improving mechanical and thermal properties as well as proton conductivity [16–19]. In this research work, polymer membranes silicon-containing sulfonated polystyrene/acrylate (Si-SPS/A) were synthesized by emulsion polymerization method followed by polymerization carried out in the presence of different percentages of ionic liquid and compare the properties of the synthesized membranes [5]. Due to the unique properties of ionic liquids can expected that synthetic membrane characteristics such as water uptake, resistance to the passage of methanol, proton conductivity and thermal stability change.

Experimental

Materials

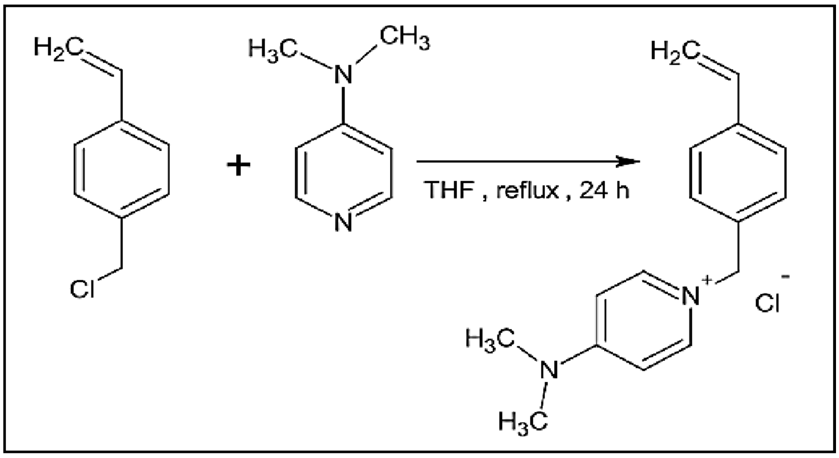
N, N-dimethylamino pyridine (DMAP) and 4-vinylbenzyl chloride obtained from MerckCompanyand used for the synthesis of ionic liquid. Styrene monomer with high purity purchased from Merck Company (Co) and used without distillation. Styrene should be kept at low temperature.2-hydroxyethyl methacrylate (HEMA), Butyl acrylate (BA) and methacrylic acid (MAA) were obtained from Merck Co. BA were distilled under an argon atmosphere and reduced pressure prior to polymerization. HEMA and MAA used without purification. Vinyltriethoxysilane

(VTES), 1, 6-hexanediol diacrylate and 4-styrenesulfonic acid, sodium salt hydrate (Na_2S, 99%) purchased from Sigma-Aldrich Company and used as received. Potassium persulfate used without further purification.The water used in this experiment distilled followed by deionization. THF (tetrahydrofuran) solvent that is used should be dry before using it.

Methods

Synthesis of polymer electrolyte membranes containing ionic liquid

N-(4-Vinyl benzyl)-4-(N, N-dimethylamino) pyridinum chloride was synthesized by the method shown in scheme 1 [20].

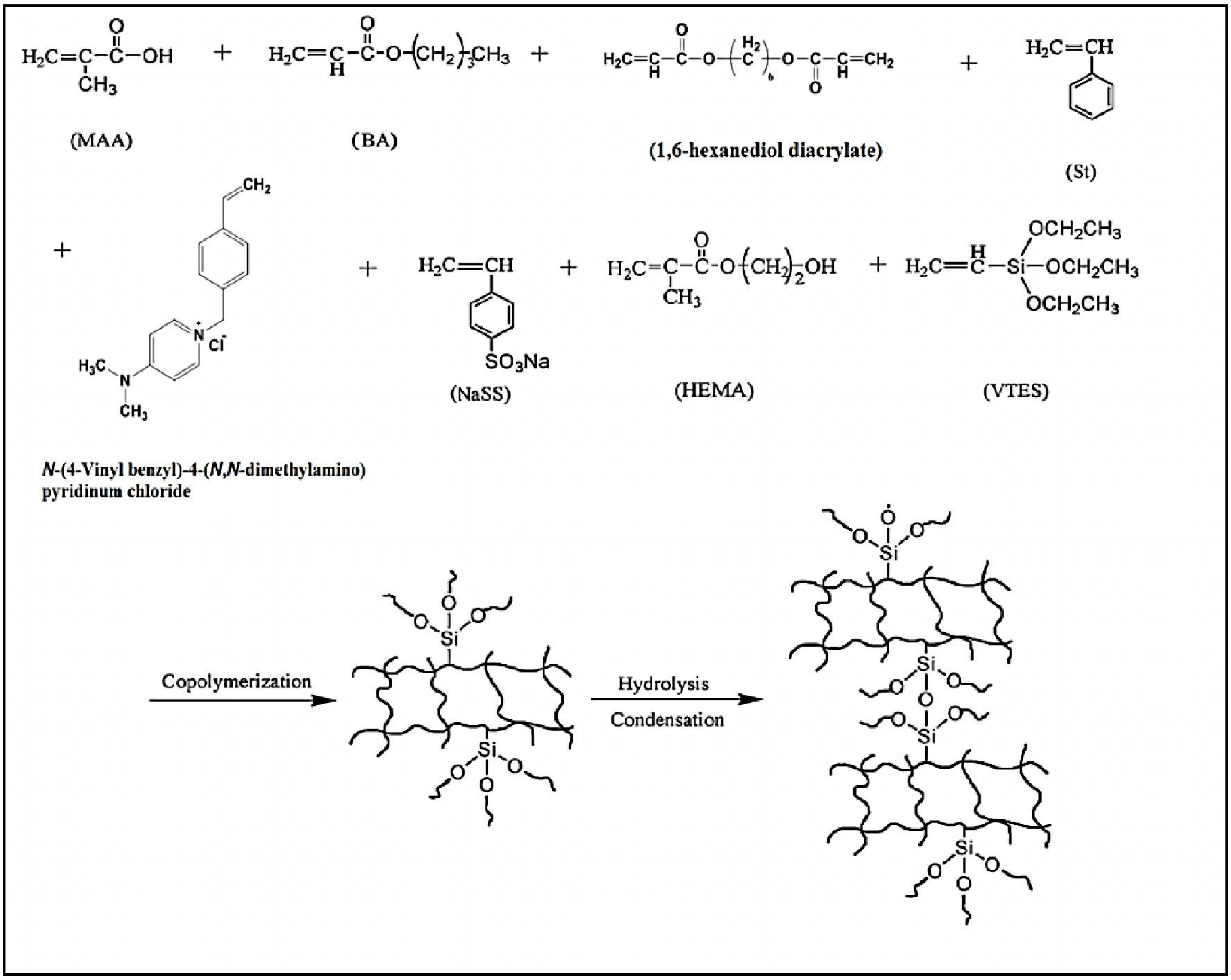


Scheme 1. Synthesis of IL (N-(4-Vinyl benzyl)-4-(N, N-dimethylamino) pyridinum chloride).

The Si-SPS/A nanoparticles synthesized via emulsion polymerization method. The polymerization carried out in a 250-ml four-neck flask that was argon-purged, equipped with reflux condenser, mechanical stirrer, dropping funnel and nitrogen inlet. First, an appropriate amount of IL and 0.5 grNa_2S introduced into the flask charged with 35 ml of deionized water, and the so-obtained solution stirred until the IL and Na_2S completely dissolved. Then, the mixture of an appropriate amount of St, 3.6 g of BA, 0.25 g of 1,6-hexanediol diacrylate, 0.92 g of VTES, 0.51 g MAA, and 10.5 g of HEMA was added into the flask. The flask placed in water bath and heated to 75˚C with a stirring rate of 300 rpm. After additional 30 min equilibration time, the aqueous solution of potassium persulfate (0.1 g of potassium persulfate solved in 5 ml water) was dropped into the above flask in 1 h and the final mixture was reacted at75˚C until the reaction mixture became white to blue. Subsequently, the temperature rise to 80˚C and maintained at this temperature for 1 h. After cooling to room temperature, the obtained latex purified from the unreacted monomers by repeateddialysis. The emulsion polymerization reaction and silica cross-linking was shown in scheme 2. Five different compounds synthesized in this way. Monomers values for each compound are list in Table 1.

Table 1. Monomer for the synthesis of I to V.

	I	II	III	VI	V
St (gr)	0.9	0.81	0.72	0.63	0.54
BA (gr)	3.6	3.6	3.6	3.6	3.6
MAA (gr)	0.51	0.51	0.51	0.51	0.51
VTES (gr)	0.92	0.92	0.92	0.92	0.92
1,6-Hexanediol diacrylate(gr)	0.25	0.25	0.25	0.25	0.25
News (gr)	0.5	0.5	0.5	0.5	0.5
HEMA (gr)	0.5	0.5	0.5	0.5	0.5
IL (gr)	0.0	0.24	0.47	0.71	0.95



Scheme 2. The emulsion polymerization reaction and silica crosslinking.

Membrane preparation

First, the nanoparticle latex obtained in the previous step was poured to a glass plate and dried in oven at 60˚C for 10 h and 120˚C for 2 h [5]. After cooling to room temperature, the resultant membrane peeled from the glass substrate and immersed in 1.0MHCl solution for 2 days. The membrane rinsed repeatedly with deionized water to remove any excess acid and stored in deionized water for further analysis.

Characterization

The Fourier Transfer infrared (FT-IR) analysis performed for all samples by KBr pellets in the range from 4000 to 400 cm^{-1}.

Thermo-gravimetric Analysis (TGA), Energy-Dispersive X-ray spectroscopy (EDX) and Differential Scanning Calorimetry (DSC) measurements performed.

The water uptake was determined as follows. The membrane dried at 100 °C until constant weight obtained (W_{dry}). The dried membrane equilibrated in deionized water for 24 h at different temperatures. Subsequently, the membranes taken out and weighed (W_{wet}) after removing surface water with filtration paper. The water uptake calculated using the following equation (1):

$$\text{Water uptake}=\frac{W_{wet}-W_{dry}}{W_{dry}}\times 100 \tag{1}$$

The methanol diffusion coefficient was determined using a glass diffusion cell (Figure 1). This cell consisted of two compartments and membrane clamped between the two compartments. First, the membrane hydratedin deionized water for at least 24 h. Then the hydrated membrane clamped between the two compartments (A and B) of a testing cell. Compartments A and B initially contained 2 M methanol solution and distilled, deionized water, respectively. Both closed compartments magnetically stirred during the experiment. The increases in concentration of methanol in the water compartment with time were measured using gas chromatography (GC). The methanol diffusion coefficient calculated as follows:

$$C_B(t) = \frac{A}{V_B}\frac{DK}{L}C_A(t-t_0) \tag{2}$$

Where A, L and V_B are the effective area, the thickness of the membrane and the volume of permeated compartment, respectively. C_A and C_B are the methanol concentration in feed and in permeated compartments, respectively. DK is the methanol diffusion coefficient.

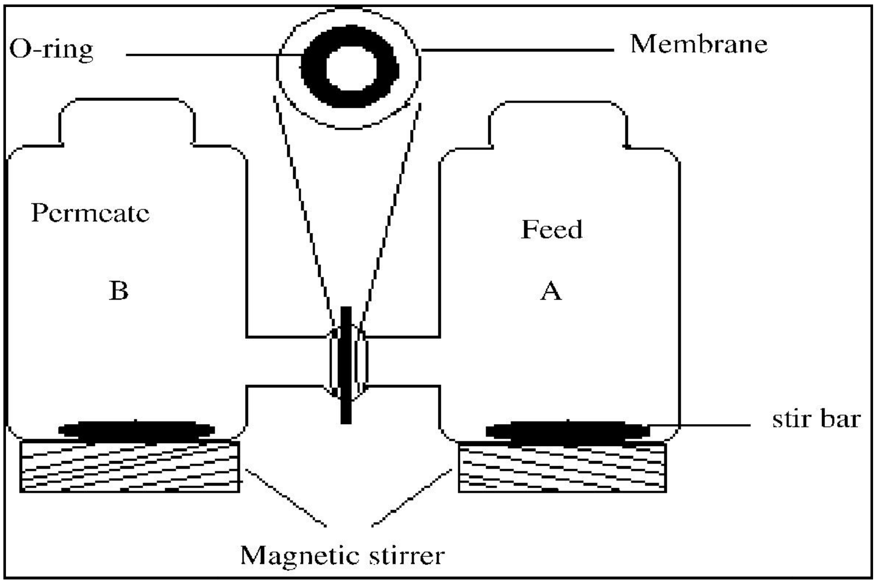


Figure 1. Glass diffusion cell.

The theoretical Ion Exchange Capacity (IEC) value calculated as the quotient of the molar content of the sulfonic acid groups and the membrane weight in feed. The titrated IEC value was determined as follows. The membrane in acid form immersed in 1.0M NaCl solution for 24 h to replace the protons of sulfonic acid groups with sodium ions. Then the replaced protons were titrated using 0.01M NaOH solution. The IEC calculated according to the equation:

$$\mathrm{IEC} = \frac{\mathrm{C}\times\mathrm{V}}{\mathrm{M}} \times 100 \qquad (3)$$

C and V are the normality and the volume of NaOH solution, respectively. M is the weight of membrane.

Proton conductivity of the proton exchange membranes measure by the electrochemical impedance spectroscopy method over the frequency range of 10 Hz-10 MHz with 50-500 mV oscillating voltage in the particular conductivity cell. Membrane sample equilibrated in deionized water for 24 h at room temperature prior to testing. Then the hydrated membrane was sandwiched between two electrodes and placed in a temperature-controlled cell containing distilled deionized water. Then, proton conductivity of membrane, s (Siemens per centimeter (S/cm)), was calculated according to equation (4), where s is defined as the reciprocal of R and L and S are the thickness and area of the membrane, respectively.

$$\sigma = \frac{\mathrm{L}}{\mathrm{R}\times\mathrm{S}} \qquad (4)$$

Results and discussion

FT-IR spectra study

The chemical structures of membranes characterize by FT-IR (Figure 2).All the samples exhibit the characteristic asymmetric stretching peaks of C–H (CH_2) at 2959 and 2936 cm^{-1}, symmetric stretching of C–H (CH_2) at 2876 cm^{-1}, stretching vibrations CH of the aromatic ring at 3027 and 3061 cm^{-1}, stretching vibration of C=O at 1733cm^{-1}, and distortion vibration of CH_2 at 1453 and 1396 cm^{-1}.The characteristic peak at 1116 cm^{-1} (characteristic of the asymmetric Si–O–Si stretch) indicated the occurrence of hydrolysis and condensation reactions of $Si(OR)_3$groups and the formation of cross-linked silica network structure in the membranes. The absorption peak at 1031 cm^{-1} ascribed to the symmetric stretching vibration of SO_3. Furthermore, the broad peak at around 3440cm^{-1} corresponded to –OH stretching vibration owing to the presence of SO_3H groups and absorbed water. In addition to the above mentioned peaks, sharp peaks at 1571 and 1649 cm^{-1} related to stretching vibrations of the C=C bond in the pyridine ring and the C-N stretching vibration in 1224 $cm^{-1}$was obtained. This represents the successful synthesis of membranes containing ionic liquid.

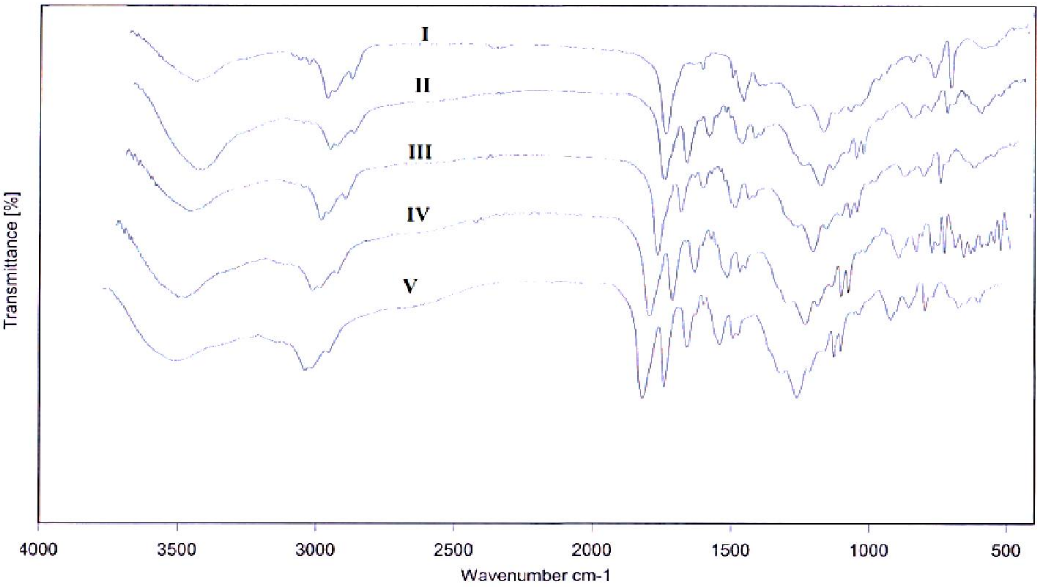


Figure 2. FTIR spectra of membranes.

EDX analysis

To determine the presence of IL molecules in the hybrid membranes, EDX use to analyze the elements in pure membrane and membranes containing ionic liquid (Figure 3). Figure 3 (A) clearly showed that the pure membrane consisted of C, O, S, Na and Si elements. Compared with Figure 3

(A), the EDX spectrum of hybrid membrane exhibited a new peak of N and Cl atoms, which demonstrated that the IL incorporated into the hybrid membrane.

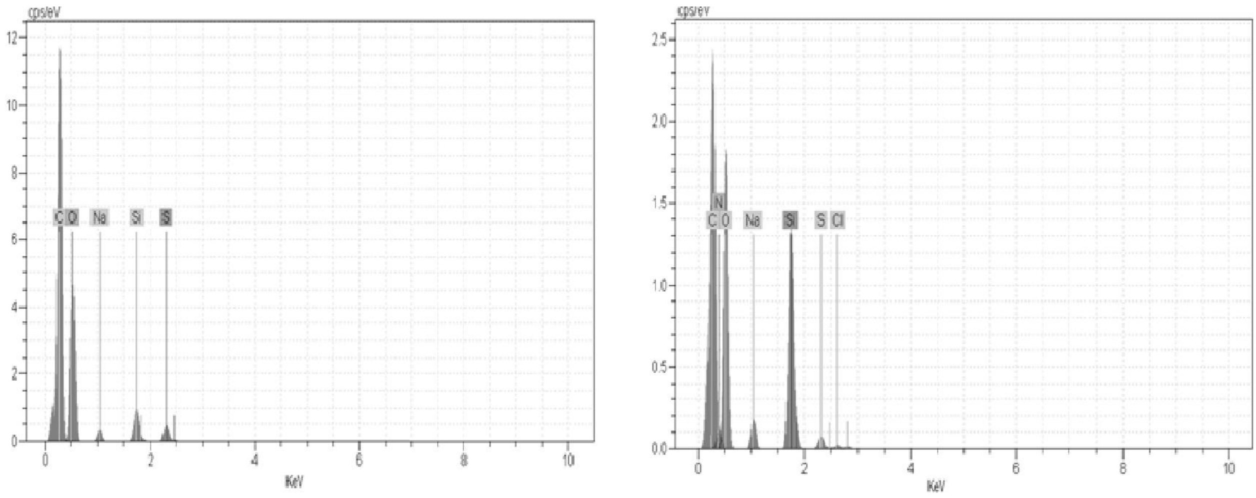


Figure 3. EDX spectra for (A) pure and (B) containing ionic liquid membranes.

Thermal stability

The thermal stability of the Si-SPS/A and hybrid membranes analyze by recording the TGA curves as shown in Figure 4. It was obvious that all the membranes exhibited a two-step degradation curve. The first degradation step between260 °C to 400 °C corresponded to the decomposition of sulfonic acid groups. The second degradation step above 400 °C assigned to the decomposition of the main chain and cross-linking bridge. When IL incorporated into the Si-SPS/A matrix, the thermal stability of Si-SPS/A decreased. Although the addition of IL caused the membrane to decompose at relatively lower temperature, the hybrid membranes still had good thermal stabilities below 300 °C, which could satisfy the requirement of PEMs in DMFCs.

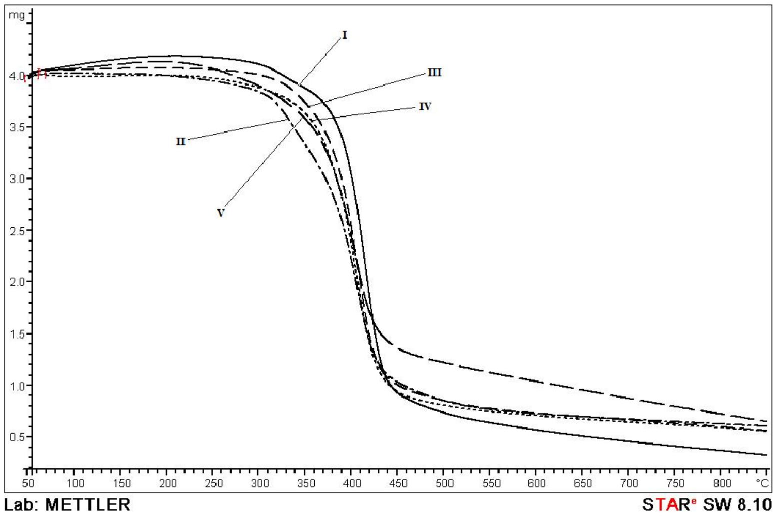


Figure 4. TGA curves membranes.

Ion exchange capacity (IEC) measurement by using of the titration method

Figure 5 shows the values of the ion exchange capacity of the synthesized membranes.

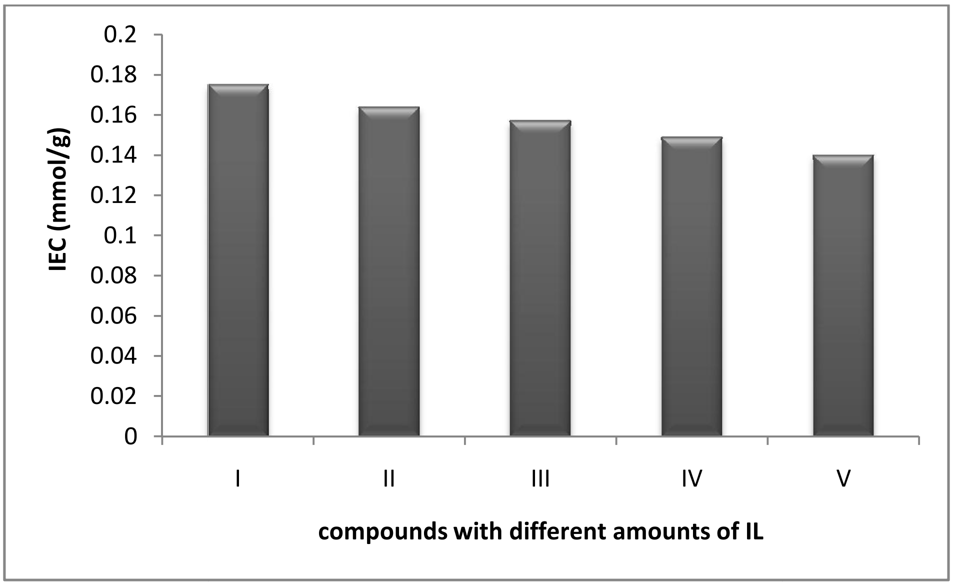
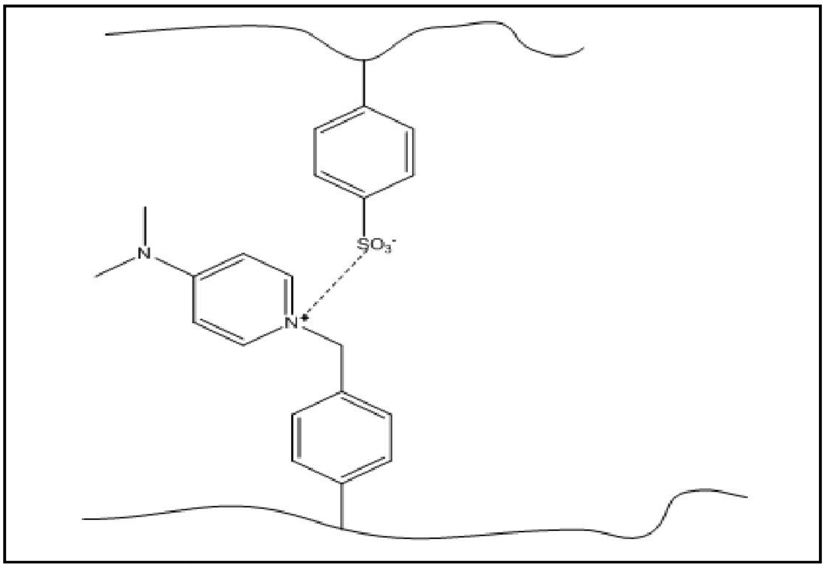


Figure 5. Ion exchange capacity of the synthesized compounds.

IEC is the measure of relative concentration of acid groups within polymer electrolyte membranes. Proton conductivity and water uptake both rely heavily on the concentration of ion conducting units (most commonly sulfonic acid) in the polymer membrane. In addition, the IEC values observed by titration method were lower than the corresponding theoretical values. This discrepancy explained by two facts in our system. On the one hand, the amount of NaSS in the final polymer maybe less than the value in the feed due to part of NaSS monomers or oligomers from the solution were not incorporated in the final particles. On the other hand, the hydrolysis and condensation reactions of Si (OR) $_3$groups in membrane led to the formation of cross-linked silica network structure. The cross-linked network decreased chain mobility and made the membrane denser and free volume depressed, which may result in less and smaller hydrophilic channels for proton mobility, and perhaps some of the groups buried inside the particles were not accessible to the reagent. In addition, electrostatic interaction between negatively charged sulfonic acid groups and positively charged ionic liquid cations reduce the IEC (Scheme 3). Hence the exchangeable –SO_3Na groups were reduced and IEC values decreased.



Scheme 3. Electrostatic interaction between sulfonic acid groups and ionic liquid.

Water uptake

The water uptake is an important property because it has a profound effect on the proton conductivity and mechanical stability of PEMs. High proton conductivity supported by high level of water uptake; at the same time, it is also a sign of low-dimensional stability as water influences the polymer microstructure and mechanical properties. Since water also known to assist the mass transport of methanol and oxygen through the membrane, the water uptake measurements could serve as a quantitative measure of membrane performance for DMFC application as well. The water uptake of membranes measured at different temperature and the results presented in Figure 6.

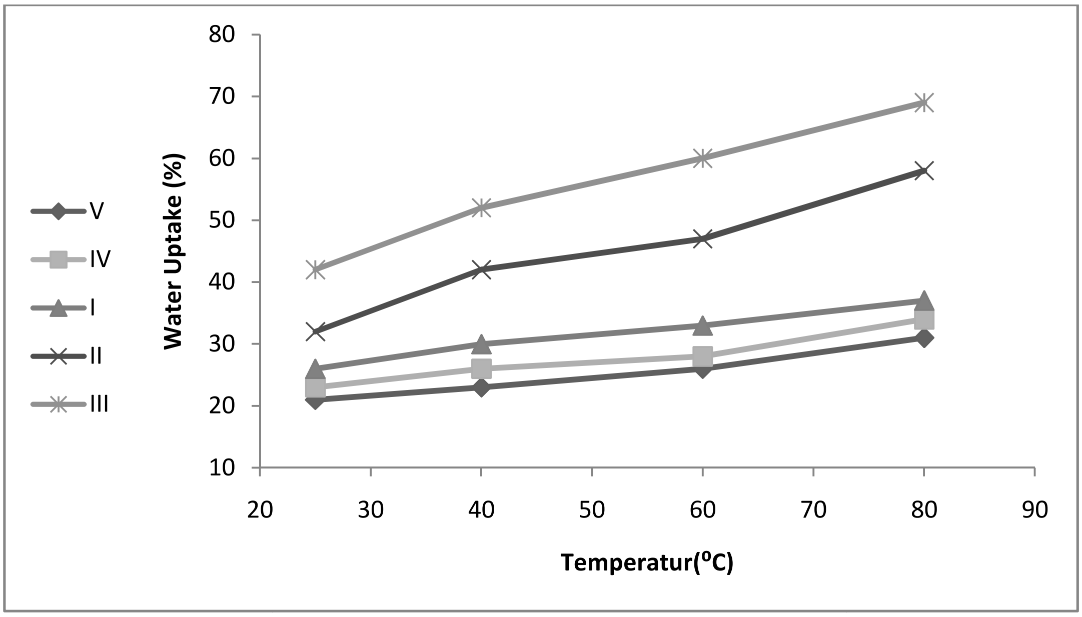


Figure 6. Water uptake of membranes at different temperatures.

Obviously, the water uptake of all the membranes displayed an increasing tendency with the increment of temperature. It understood because when the temperature elevates, the polymer chain mobility and the free volume for water adsorption increase, which result in the increase in water uptake. In addition, it is note that compared with Si-SPS/A membrane, water uptake of hybrid membranes first increased and then decreased with the increment of IL content.

Several factors might affect the water uptake of hybrid membranes:

- The introduction of IL could increase the water uptake of membranes due to the hydrophilic properties of ionic liquid.
- A part of free volume of membranes occupied by IL molecules, which enhance compactness of membranes and limit the space absorbed water molecule.
- The interaction between Si-SPS/A and IL could reduce polymer chain mobility and free volume, which leads to more rigid and compact structure in the hybridmembranes and hence decreases water uptake.From the result ofwater uptake, it concluded that in the II and IIImembranes, the hydrophilic character of IL played a dominant rolefor the change of water uptake. However, at higher IL content (IV and V) the latter two factors were more prominent than the hygroscopic effect.

Methanol diffusion coefficient measurement

The study of the methanol mass transport through DMFC membranes is very common due to its detrimental effect on the DMFC performance. In DMFCs, the methanol diffusion not only wastes fuel but also results in the significant loss of fuel cell performance. Hence, the PEMs used in DMFCs should possess low methanol diffusion coefficient. Table 2 lists the methanol diffusion coefficient of membranes. When hydrophilic IL groups incorporated into the membranes, II and III compounds form more and larger water absorption channels. Hence, methanol could easily go through the channels and methanol diffusion coefficient enhanced correspondingly. However, because of the low water absorption of compounds IV and V, methanol diffusion coefficient consequently reduced. The lowest methanol diffusion coefficient measured from V membrane, indicating that the incorporation large amounts of IL to Si-SPS/A matrix could cause the decrease of methanol diffusion across the membrane and the hybrid membranes could serve as one kind of materials with extremely low methanol crossover in DMFCs.

Table 2. Proton conductivity, methanol diffusion coefficient and selectivity of membranes at 25 °C.

Membranes	Methanol diffusion coefficient (cm^2s^{-1})	Proton conductivity (Scm^{-1})	Selectivity ($Sscm^{-3}$)
I	1.82×10^{-8}	2.18×10^{-3}	1.20×10^{3}
II	2.29×10^{-6}	7.32×10^{-3}	3.20×10^{3}
III	0.762×10^{-6}	1.43×10^{-2}	1.88×10^{4}
IV	1.79×10^{-8}	1.94×10^{-3}	1.08×10^{5}
V	1.52×10^{-8}	1.73×10^{-3}	1.14×10^{5}
Nation 117	2.36×10^{-6}	5.02×10^{-2}	2.13×10^{4}

Proton conductivity

Proton conductivity is a critical property of fuel cell membranes. The proton conductivity data of hybrid membranes as a function of IL content at 25 °C listed in Table 2. The proton conductivity of these membranes depended on various factors. First, it noted that proton conductivity increased with increasing IEC and water uptake. It is because those protons transferred between ionic clusters consisting of polar groups such as $–SO_3H$ and the number of ionic clusters related to the number of $–SO_3H$ groups and water content in the membrane.

Incorporating IL molecule to the Si-SPS/A matrix might have several effects on the proton conductivity of hybrid membranes. The first effect is to increase the concentration of H^+ (the ratio of amount of H^+ to water content), which could be proved by the results of water uptake measurement. Generally, increasing the charge density can decrease the energy barrier for charge transport, which is favorable for the improvement in proton conductivity. The second effect is to block/reduce the proton migration channels due to the interaction between Si-SPS/A and IL (Scheme.3).It found that the proton conductivity of hybrid membranes increased with increasing amount of IL in II and III compounds while compounds IV and V with an increase in the IL, the proton conductivity decreases.

Selectivity

The selectivity (ratio of proton conductivity to methanol diffusion coefficient) used to compare the applicability of proton exchange membranes. The higher the selectivity value, the better the membrane performance is. The selectivity for different membranes at 25 °C present in Table 2. It can been noted that though the IV and V membranes displayed lower proton conductivity, they offered higher selectivity in comparison with Nafion® 117 membrane due to tremendous reduction in methanol diffusion coefficient.

Conclusion

Proton-conducting hybrids from Si-SPS/A and IL were prepared and their suitability as PEMs for DMFC applications investigated. Results show that the hybrid membranes are promising candidates for PEM applications in DMFCs. In future studies, other ionic liquid used in the membrane structure and examined the results.

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