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Research Paper

Preparation of anionic-exchange membranes composites for acid recovery from acidic wastewater

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ABSTRACT

This study aimed to prepare the anion exchange membrane (AEM) from brominated poly (2, 6-dimethyl-1, 4-phenylene oxide)/polypyrrole (BPPO/Ppy) composites, and to study the effects of pyrrole (Py) concentrations and amination reaction on conductivity and transport properties of the membranes. The 8 wt% PPO was reacted with 20 wt% Br_2 in chlorobenzene solutions at a control temperature of 131℃. The obtained product was characterized by FTIR and H-NMR to confirm the benzyl bromination on PPO. BPPO membranes were prepared by solution casting method (thickness 0.45 - 0.5 mm). The BPPO/Ppy composites were prepared by soaking the BPPO membrane in Py solution (vary from 0.3 – 0.5 mol dm^{-3} for 24 hr. The ion exchange capacity (IEC), water uptake (W_R) and conductivity of the membranes were investigated. The effects of amination reaction with 0.5 mol.dm^{-3} trimethylamine (TMA) were also studied. The results showed that ion exchange capacity (IEC), conductivities and water uptake and acid permeability of composite membranes were enhanced by amination reaction. However, the BPPO/Ppy composite membrane without TMA amination was found to provide the better acid diffusion coefficient than that with TMA. Further investigations should focus on fine tuning the conditions to obtain high hydrophilicity, water uptake and ion selectivity rejection.

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1. Introduction

The development of synthetic ion exchange membranes had been reported since 1950s (Hong et. al., 2008). The traditional ion exchange membranes are classified into anion exchange membranes (AEMs) and cation exchange membranes (CEMs) depending on the type of ionic groups attached to the membrane matrix. Typically, CEMs contains negatively charged groups, such as $–SO_3^-$, $-COO^-$, $-PO_3^{2-}$, $-PO_3H^-$ etc. Examples of their applications are fuel cell technology and redox flow battery applications (Kristensen et al., 2016). The applications of AEMs are widely used in the electrodialysis for the desalination of brackish water, recovery metal ions from the effluents of metal-plating industry etc (Tongwen and Zha, 2002). One of the major applications of AEM is acid recovery where AEM is equipped in diffusion dialysis unit (DD). Proper properties of the AEM are also necessary, including stability in acidic solution, high H^+ permeability, and strong rejection for other metal ions (Jingyi et al., 2011). The advantage of DD process is known from its higher efficiency in purifying wastewater, low energy consumption and easy for operation (Jingyi et al., 2011). However, the restriction of DD process is the equilibrium concentration and the processing capability is relatively low (Xu, 2004). Besides, the long-time running stability of DD process depends largely on the strength and stability of the ion exchange membranes (Jingyi et al., 2010). The prerequisites of an anion-exchange membrane utilized in the DD process are high acidic resistance of the membranes, high proton permeability but strong rejection of metal ions and relatively high water content but poor water permeability (Zu and Yang, 2004; Zu and Yang, 2001).

Anion exchange membranes contains positively charged groups, such as $–NH_3^+$, $–NRH_2^+$, $–NR_2H^+$, $–NR_3^+$, $–PR_3^+$, $–SR_2^+$, etc., fixed to the membrane backbone and allow the passage of anions but reject cations (Tongwen, 2005). The strongly basic anion exchange membrane is usually prepared by two steps, i.e. chloromethylation and quaternary amination (Kesting, 1985). In the chloromethylation, the used chloromethyl methyl ether is a carcinogen and is potentially harmful to human health (Lin and Takai, 1994). Until now, ion-exchange membranes have been developed mostly by using several engineering polymers such as polystyrene, polysulfone, poly (vinyl alcohol), poly (ether ether ketone), and poly (2, 6-dimethyl-1, 4-phenyleneoxide) (PPO) as a backbone material to improve the membrane properties such as the ion transport and selectivity (Park, 2014). A new series of anion exchange membranes with both good electrochemical properties and excellent dimension stability have been initiated in our laboratory, which were also directly made from engineering polymer poly (2,6-dimethyl-1,4 phenylene oxide) (PPO) by bromination and simultaneous amination-crosslinking processes but no chloromethyl methyl ether is used (Tongwen and Zha, 2002). There have been several attempts to modify of the ion exchange membranes to improve the membrane properties such as the ion transport and selectivity. Zeng et al. examined effects of polypyrrole (Ppy) coating on the interfaces of Nafion membranes (Kim et al., 2014). There has been a report on comparison study between Ppy and polyaniline coatings on Nafion membranes in terms of transport properties. The nitrogen heteroaromatic pyrrole rings in Ppy become protonated under the strongly acidic conditions of the diffusion test solutions. Thus, Ppy was expected to form a cationic blocking layer for metal ions (Kim et al., 2014). However, the poor processability of conducting polymers was found to be a major disadvantage in their extensive applications. Out of several methods, the preparation of conducting polymer composites by chemical oxidative polymerization has been used to improve processability, which is the problem of the conducting polymer (Lee et al., 2004).

For these reasons, we attempt to prepare a new series of anion exchange membranes directly from engineering polymer and examined the influence of membrane preparation conditions on the membrane properties including ion exchange capacity (IEC), conductivity, water uptake (W_R) etc.

2. Materials and methods

2.1 Materials

Poly (2, 6-dimethyl-1, 4-phenylene oxide) (PPO), bromine (Br_2), chlorobenzene (CB), chloroform, trimethylamine (TMA) and sulfuric acid were purchased from Merck. All the chemicals were analytical grade.

2.2 Preparation of anion exchange membrane

Brominated PPO was prepared using the method modified from Park et al. (2014); an 8 wt% solution and then a bromine solution (20 wt% Br_2 in CB) were slowly added into the PPO/CB solution for the bromination. The Br_2: PPO mole ratio was fixed at 1:1 and the reaction was conducted with vigorous stirring at 131 ± 2 ℃ for 10 hr. Then, this solution was precipitated with methanol and the precipitated polymer was dried in a vacuum oven at 80 ℃ for 1 day to get benzyl-substituted polymer (BPPO) (Tongwen et al., 2005). The obtained product was characterized by FTIR and H-NMR to confirm the benzyl bromination on PPO.

The membrane composites were prepared by solution casting method. The BPPO powder was dissolved in chloroform to form an 8 wt% solution with vigorous stirring at room temperature for 24 hr. The solution (BPPO in chloroform) was cast onto a petri dish substrate to form a base membrane of 0.45 - 0.5 mm dried thickness. This base membrane was first immersed in Py solution for 24 hr. The concentrations of Py solution was varied in a range of 0.03 - 0.5 mol dm^{-3}. The composite membranes were then prepared by oxidative polymerization using ammonium persulfate as an oxidant and HCl solution as a dopant. The polymerization was allowed at room temperature for 24 hours. The mole ratio of oxidant to dopant to Py was fixed at 1.25: 0.5: 1. For a comparison, several flat BPPO membranes were immersed in TMA aqueous solution. The concentration of TMA was fixed at 0.5 mol dm^{-3}. All of the membranes were stored in 1.0 mol.dm^{-3} NaCl for over 1 day. Then, the filter paper (GF/C) was used to adsorb excess liquid on the membrane surface. The membranes were then kept dry in the desiccator until the weight unchanged. The amount of Ppy formed inside each membrane was determined by the differences in weights (dry basis) before and after polymerization (Hong and Wang, 2008).

2.3 Membrane characterizations

The obtained membranes were characterized by intrinsic properties such as the ion exchange capacity (IEC, mmol/g dry membrane), water uptake (W_R, %) and conductivity (S/cm) as follows.

To determine the IEC, the dry membrane was weighed and immersed in 1.0 mol.dm^{-3} NaCl more than 1 day. The membranes in a Cl^- form were then converted to the SO_4^{2-} form by immersing the membrane in 0.5 mol.dm^{-3} Na_2SO_4 for 2 days. The amounts of chloride ions exchanged by SO_4^{2-} ions were determined by titration the Na_2SO_4 solution with 0.005 M $AgNO_3$ solution using K_2CrO_4 as an indicator. The IECs were calculated and given as mmol/g dry membrane. The water uptake (W_R) was determined after equilibrating samples in 1 mol.dm^{-3} NaCl solution more than 1 day at room temperature. The composite membranes were kept in a desiccator and accurately weighed to confirm their exact dry weight. Then, the membranes were immersed in distilled water for 2 days at room temperature. The wet weights of those membranes are recorded after a step of excess water removal with filter paper. W_R values were measured as the relative weight gain per gram of the dry sample using the following equation.

$$W_R = \frac{W_{WET} - W_{DRY}}{W_{DRY}} \text{ x } 100\% \qquad [1]$$

Where; W_{WET} and W_{DRY} are the weights of wet and dry membranes respectively.

The conductivity of the membranes was measured by using four-point probe technique with auto lab under the current of 100 nA.

Diffusion dialysis was evaluated using a two-compartment cell of equal volume (240 mL) separated by the composite membranes (apparent area: 4 cm^2). The side of feed cell was filled with the mixture solution of H_2SO_4–$FeCl_3$, and the permeate side with distilled water. During the diffusion test, both compartments were vigorously stirred to minimize a concentration polarization effect. Sampling of the permeate solution was carried out by every 2 hr to measure the acid concentration. The proton concentration in the solutions was determined by an acid-base titration. All experiments were performed at room temperature. The dialysis coefficients (U_H) can be calculated by the following formula.

$$U_H = \frac{M}{A\,t\,\Delta C} \qquad [2]$$

Where; M is the amount of component transported in moles, A the effective area in square meters, *t* the time in hr, and ΔC the logarithm average concentration between the two chambers in moles per cubic meters. ΔC is calculated as below:

$$\Delta C = \frac{C_f^0 - (C_f^t - C_d^t)}{\ln[\frac{C_f^0}{C_f^t - C_d^t}]} \qquad [3]$$

C_f^0 , C_f^t are the feed concentration at time 0 and *t*, respectively and C_d^t is the dialysate concentration at time *t*. (Congliang et al., 2014)

3. Results

3.1 The bromination processes

The base membranes were prepared from brominated PPO with polymer solution. It was expected that the introduction of bromine on the PPO can effectively increase the proton leakage through the membranes. The brominated PPO was confirmed from the FT-IR spectra as shown in **Fig. 1**.

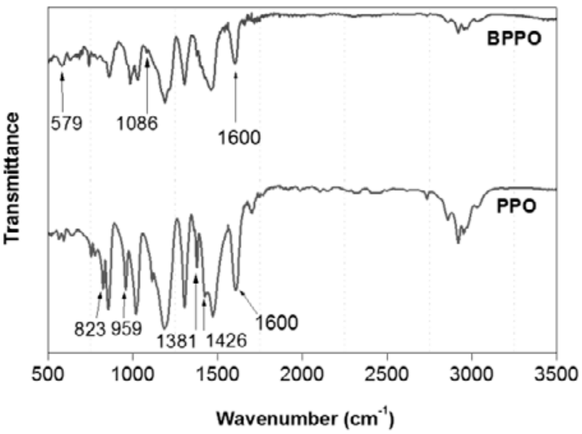

Fig. 1. FT-IR spectra of PPO and BPPO powder.

The absorption peak assigned to the C-Br symmetric stretching was observed in the wavenumber of 579 cm^{-1} in the BPPO sample. For both PPO and BPPO, the absorption peaks assigned to the stretching and bending vibration of C-H bonds were observed at 1381cm^{-1} and 1426 cm^{-1}, respectively. Moreover, the absorption bands at 824 – 1019 cm^{-1} and 3000 - 3100 cm^{-1} were ascribed to bending of alkene and stretching of C-H from benzene rings respectively. Peak at 1600 cm^{-1} was the stretching of C=C bonds. The bending vibration of C-H from CH_3 disappeared at 1381 cm^{-1} due to benzyl substitution of bromine which confirmed the existence of $–CH_2Br$ due to bromine substitutions

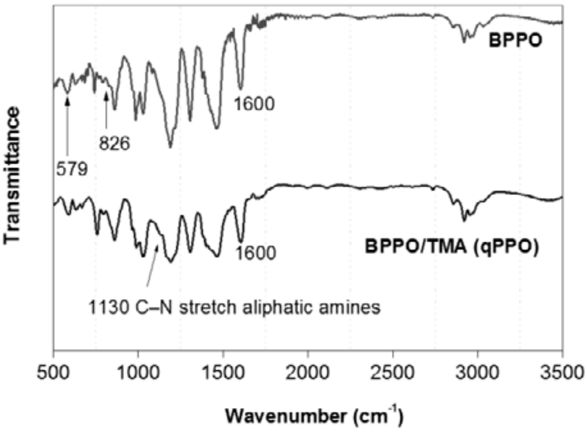

Fig. 2. FT-IR spectra of the BPPO and qPPO membranes.

FT-IR spectra of the BPPO membrane before and after amination reaction with 0.5 mol dm^{-3} TMA aqueous solution (qPPO) are shown in **Fig 2**. The characteristic peaks of qPPO membrane were similar to those of the BPPO membrane and BPPO powder except the peak corresponding to C-N bond stretching at 1130 cm^{-1}. The existence of the peak at 1130 cm^{-1} proved the presence of quaternary-ammonium ion ($+N(CH_3)_3$) in polymer structure. Thus quaternized BPPO membrane (qPPO) was successfully prepared. Other characteristic peaks of qPPO were analyzed and compared with those of PPO and BPPO as shown in **Table 1**.

Table 1. FT-IR spectrum analysis of PPO, BPPO and qPPO.

Functional groups	Wavenumber (cm^{-1})		
	PPO	BPPO	qPPO
C – Br (st)	-	579	-
C – N (aliphatic amine) (st)	-	-	1130
C – H (1,2-disubstituted) (b)	754	753	757
C – H (1,3 disubstituted) (b), (1,2,4-trisubstituted) (b)	855	860	860
C = C (alkene) (b)	959	985	971
C = C (alkene) (st)	3030	3032	3029
C – O – C (st)	1026	1031	1029
	1122	1085	1085
C – O (ester) (st)	1188	1189	1192
CH_3 (aromatic) (b)	1381	1381	1390
	1426	1426	1401
CH_2 (aromatic) (b)	1475	1470	1465
CH_3 (aromatic) (st)	2859-2953	2857-2974	2858-2958
C = C(aromatic) (st)	1606	1602	1603

The bromination reaction was confirmed by ^{1}H NMR spectra. Proton resonance signals of PPO and brominated PPO (BPPO) are shown in **Fig. 3**. The peak at 6·4 ppm assigned to the aryl protons of PPO was observed. The protons due to the benzyl group appeared at 2.1 ppm as a multiplet. After bromination, new peaks attributed to the proton of bromomethyl ($–CH_2Br$) group was observed at about 4.3 ppm. Besides the bromination at methyl groups, electrophilic substitution at aromatic ring was also observed. Aryl protons at 6.4 ppm (in PPO spectrum) diminished and shifted to new positions at 6·5-7.0 ppm.

Due to the insolubility of qPPO in $CDCl_3$, the^{1}H-NMR spectrum was not recorded for qPPO.

3.2 Ion Exchange Capacity (IEC)

The effect of Ppy concentrations on the IEC of the composite membranes is shown in **Fig. 4**. As compared to the IEC of BPPO base membrane (0.08 mmol/g), it was found that the IEC of BPPO membranes significantly increased after Ppy was introduced to the membranes. This result was because of that Ppy contained the ion exchange group of $NH^+(C_4H_4)Br^-$. IEC values unchanged with Ppy concentrations with their values ranged from 1.17 to 1.18 mmol/g. This result was unexpected. The unchanged IECs upon Py concentration may be explained by the formation of the dense Ppy layer on the membrane surface. As Py concentration increased, the dense Ppy layer was easily formed. This dense layer could prevent Cl^-/SO_4^{2-} ions from further migrating to the membrane

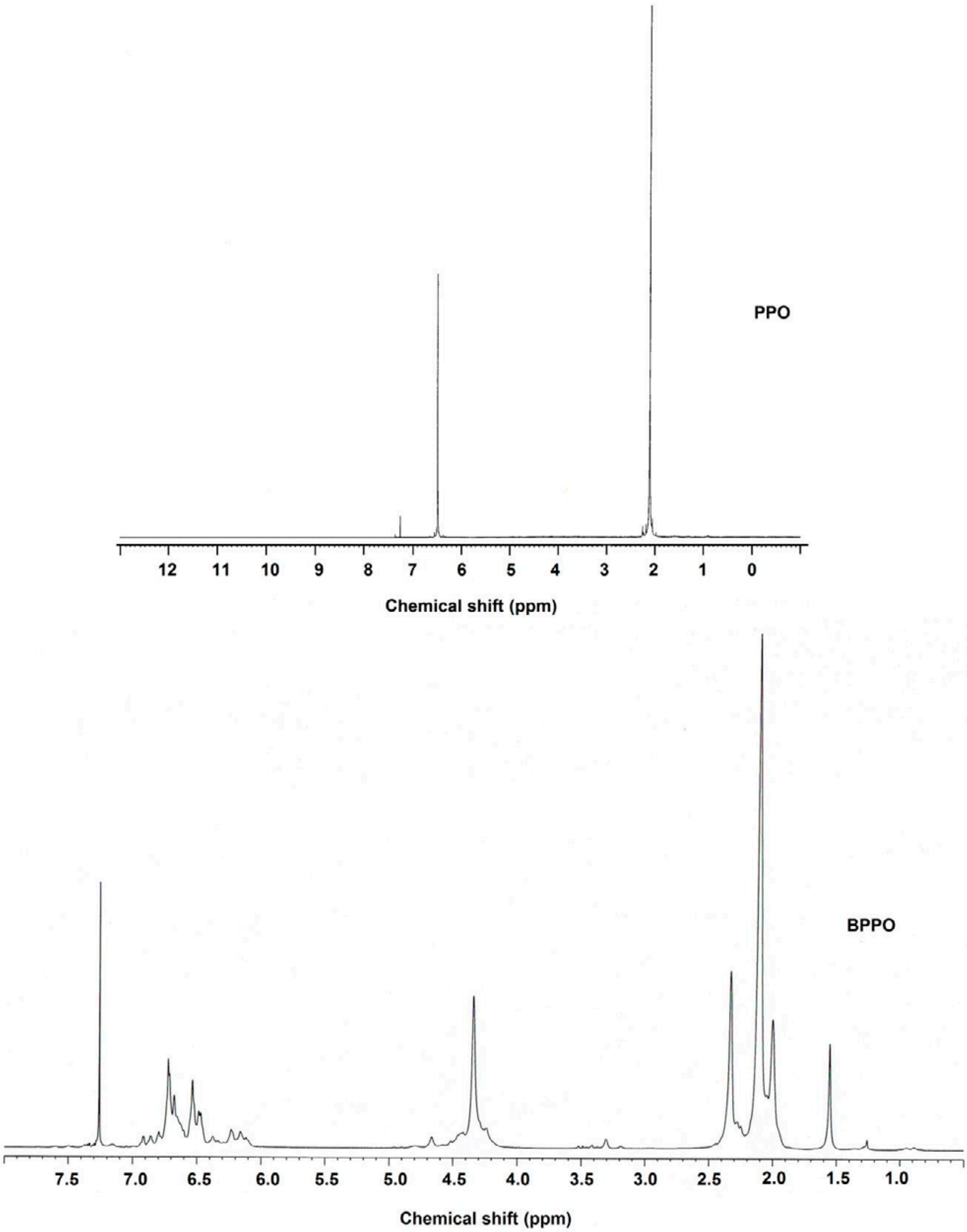

Fig. 3. ^{1}H-NMR spectra of PPO and BPPO powder.

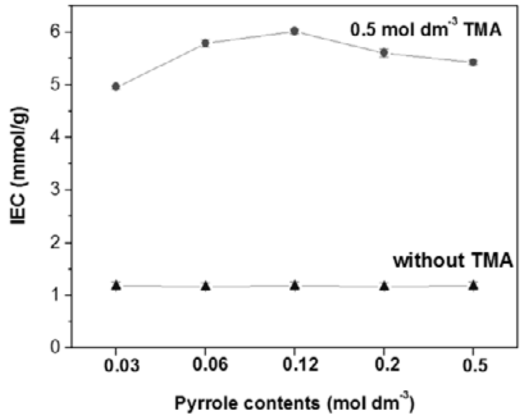

Fig. 4. Ion exchange capacity (IEC) of qBPPO/Ppy and BPPO/Ppy composite membranes.

The effect of the amination of bromomethyl groups on IEC was also studied. It was found that IECs significantly increased after the BPPO membrane reacted with 0.5 M TMA. The reasons could be based on the amination reaction as described in **Fig.5**. After TMA amination, the ion exchange group of the quaternary ammonium ions had been highly presence in the system, and thus contributed to the increase in IECs. This result indicated the successful grafting of TMA on BPPO/Ppy composite membranes. With the increases in the amounts of Py up to 0.12 M, the IEC of the aminated BPPO/Ppy composites increased. As discussed previously about the formation of the dense Ppy layer at a high Py concentration (> 0.12 M), this dense layers possibility retarded the penetration of ion (Cl^-/SO_4^{2-}), leading to the slight decreases in IECs.

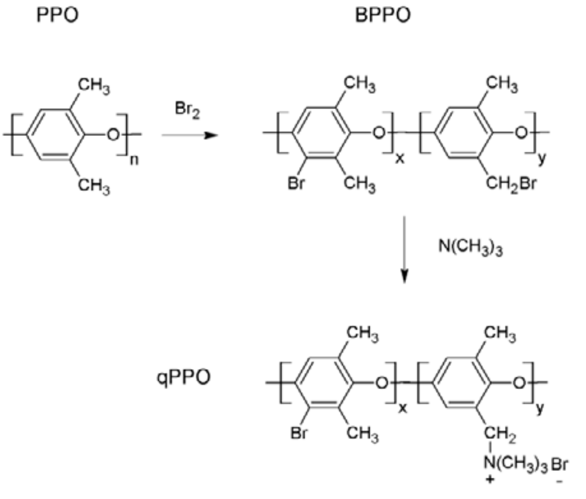

Fig. 5. The amination reaction of BPPO.

3.3 *The conductivity and water uptake*

As shown in **Fig. 6**, the conductivities of BPPO/Ppy membranes significantly increased with the increasing Ppy concentrations. The increase in the conductivity could be correlated with the increased charge densities on the membrane. After the introduction of 0.5 mol.dm^{-3} TMA on the membrane, the quaternary ammonium ions enhanced the charge densities of the composite membrane, resulting in the increases in conductivities.

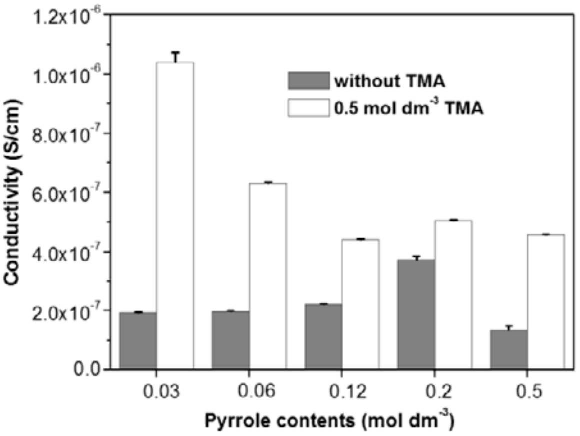

Fig. 6. Conductivity of BPPO/Ppy and qPPO/Ppy composite membranes.

With the TMA amination, the conductivities of the composite membranes decreased with increasing Py concentrations up to 0.12 mol.dm^{-3}. However, after experiencing a higher concentration of Py, the conductivity attained a plateau value at 0.12 mol.dm^{-3} Py concentrations, and remained nearly unchanged afterward. These results could be possibly explained by the formation of the dense Ppy layers which restricted the ion transport capability.

The water uptake with different concentrations of Py is shown in **Fig. 7**. It was found that the water uptake of BPPO/Ppy composite membranes (without TMA) slightly increased as the Py concentration increased up to 0.12 mol.dm^{-3}. In case of the composite membranes with TMA amination (qBPPO/Ppy), the water uptake increased significantly as the Py concentrations increased, and started decreasing after using higher Py concentrations. The highest water uptake was observed (7.58%) at 0.12 mol.dm^{-3} Py concentration. These results indicated that addition of TMA could enhance the water uptake property of the composite membranes (qBPPO/Ppy). However, their hydrophilicity could be diminished if the membranes were developed with Py concentration higher than 0.12 mol.dm^{-3}.

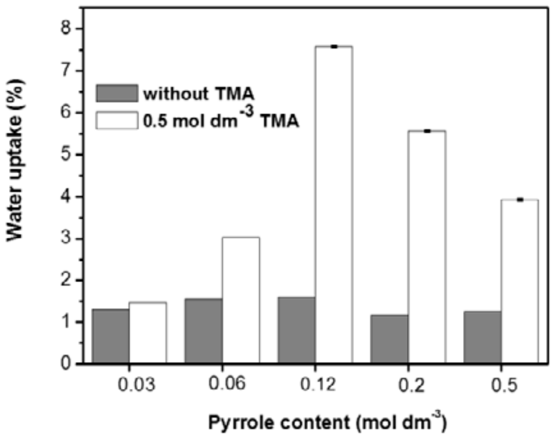

Fig. 7. Water uptake of BPPO/Ppy and qPPO/Ppy composite membranes.

3.4 *The effect of time on membrane characteristics and diffusion dialysis (DD)*

The membrane properties were significantly affected by TMA amination time. The shorter amination time (3 hr) would bring about the decreases in IEC, water uptake and conductivity as shown in **Table 2**.

Table 2. Characteristics of the BPPO/Ppy and qPPO/ Ppy composite membranes treated with 0.12 Py.

Parameters		BPPO/ Ppy	qPPO/Ppy	
			3 hr in TMA 0.5 mol.dm^{-3}	24 hr in TMA 0.5 mol.dm^{-3}
Water uptake	(%)	1.6	4.99	7.58
IEC	(mmol/g)	1.18	2.37	6.02
Conductivity	(S/cm)	4.75×10^{-8}	3.10×10^{-7}	4.42×10^{-7}
Diffusion coefficient	(m/hr)	5.67×10^{-5}	9.75×10^{-4}	NA

Moreover, the composite membrane with TMA amination time of 24 hr was too brittle to assembly in DD compartment. Thus, BPPO/Ppy composites both without and with TMA amination reaction for 3 hr were selected for DD testing. Interestingly, acid permeability was significantly affected by the amination reaction. After aminated with 0.5 mol.dm^{-3} TMA for 3 hr, the acid diffusion coefficient (U_H) values at 8 hr of DD significantly increased from 5.67×10^{-5} m/hr (without TMA) to 9.75×10^{-4} m/hr (with TMA). The increase in U_H could be probably explained as TMA amination may increase hydrophilicity of the membrane surface. This property escort favorable interfacial interactions of the H^+ species at the membrane surface. However, addition of higher TMA and Ppy may contribute to a dense layer of highly positive charges on the composite membranes (qPPO/Ppy). This dense layer may cause charge repulsion actions which could instead impede the transportation of H^+ through the membrane. As a result, the diffusion coefficient of H^+ (U_H) obtained from this study was relatively low.

4. Concluding remarks

BPPO/Ppy and BPPO/Ppy/TMA composite membranes were successfully prepared with solution casting method. The results showed that ion exchange capacity (IEC), conductivities and water uptake and acid permeability of composite membranes were enhanced by amination reaction. However, the BPPO/Ppy composite membrane without TMA amination was found to provide the better acid diffusion coefficient than that with TMA. As for acid recovery application, hydrophilicity of membrane (i.e. water uptake) seems to encourage the diffusion of H^+ through the membrane due to “vehicle mechanism” while increasing positive charges of the membrane would directly relevant to either the repulsive action on H^+ diffusion or the rejection of metal ions. Further investigations should focus on fine tuning the conditions to obtain not only high hydrophilicity and water uptake but also have a high conductivity and ion selectivity rejection. The impact of possible interferences on H^+ diffusion coefficient such as salt contents and the presence of metal ions (other than Fe^{3+}) should also be studied.

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Symbols and abbreviations

FTIR	Fourier transform infrared spectroscopy
H-NMR	Proton nuclear magnetic resonance
hr	Unit of reaction time
^{o}C	Unit of temperature
Py	Pyrrole
PPy	Polypyrrole
$CDCl_3$	Deuterochloroform
wt%	Unit of solution concentration
$mol.dm^{-3}$	Unit of solution concentration
mmol/g	Unit of ion exchange capacity
nA	Unit of the applied current
cm^{-1}	Unit of wavenumber
st	Stretching vibration
b	Bending vibration
H^+	Proton species