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Development of high performance anion exchange membranes for diffusion dialysis process

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ABSTRACT

In this article, the development of a series of low-cost anion exchange membranes (AEMs) for the diffusion dialysis process was carried out via the solution casting method. The synthesis of AEMs was confirmed by using Fourier transform infrared spectroscopy. The prepared membranes exhibited a dense structure. They showed an ion exchange capacity of 1.41–1.90 mmol/g, water uptake (W_R) of 15%–36%, and linear swelling ratio of 3.60%–21% at ambient temperature. They represented excellent thermal, mechanical, and chemical stability. The acid recovery performance of the prepared membranes was evaluated via diffusion dialysis process by employing a simulated mixture of HCl and $FeCl_2$ as model feed. At 25°C, the acid diffusion dialysis coefficient (U_H^+) was found in the range of 4.5–28 (10^{-3} m/h). Moreover, the separation factor (S) was in the range of 178–305. It showed higher diffusion dialysis performance of the prepared AEMs compared to commercial membranes DF-120 ($U_H^+ = 0.004$ m/h, $S = 24.3$) under the same experimental conditions. The influence of temperature on diffusion dialysis performance of the prepared AEMs was also revealed. Therefore, the synthesized AEMs could be employed as a good candidate for acid recovery.

Keywords: Diffusion dialysis; Anion exchange membranes; Bromo-methylated poly(phenylene oxide); Ion exchange capacity; 4-(dimethylamino)butyraldehyde diethyl acetal

1. Introduction

Various industrial processes including metal etching, pickling steps, and stripping produced a huge volume of acidic wasted solution. The serious environmental pollution and the waste of useful resources occurred by direct removal of these waste solutions. In the container system, these waste solutions cause strong deterioration. The recoverable acids and metals are present in waste solutions. Hence, from economic and environmental viewpoint, the resource application of pickling wastewater is a critical issue to be addressed [1–3]. Several methods such as pyrohydrolysis, neutralization and precipitation, crystallization, electrodialysis, and diffusion dialysis were used for the treatment of acidic waste liquors [1,4,5]. In the diffusion dialysis process, solutes from a high-concentration solution migrate to a lower concentration solution through an ion-exchange membrane under the influence of concentration gradients. Hence, there is no requirement of pressure or energy for the diffusion dialysis process. Diffusion dialysis process using AEMs has more advantages such as easy operation, low consumption of energy, environmental friendliness, and high efficiency compared to other common methods for the treatment of acidic waste solutions [6].

Ion exchange membrane (IEM) is a thin films made up of fixed positively or negatively charged moieties covalently bonded to the polymer backbone and accountable for

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exchanging moveable ions and increasing hydrophilicity into the polymer matrix [7]. IEMs can be divided into anion exchange membranes (AEMs) and cation exchange membranes (CEMs) based on the kind of ionic groups bonded into the membrane matrix. The separation of ions is dependent on the fixed charged moiety inside the membrane matrix. AEMs due to their dense nature and comfortable fabrication from distinct polymers are propitious for diffusion dialysis process. For diffusion dialysis process, AEMs should selectively allow the migration of anions across the membrane although inhibiting the migration of the cations and thus to recover acid. Because of smaller size and high mobility than other cation, the proton should cross the membranes. Usually, the AEMs were fabricated by bonding cationic head groups with the polymer backbone [8–12]. Hence, the major challenge for acid recovery and wastewater treatment is the fabrication of cost-effective AEMs with required optimum properties including long-term stability, higher selectivity, and permeation.

The polymer backbone of AEMs has a crucial influence on their properties. The stability and selectivity of AEMs are dependent on the hydrophobicity and mechanical strength. Moreover, an advanced well-connected ion-conducting channel is needed to attain the mandatory ion exchange capacity (IEC) of the AEMs which will enhance the diffusion dialysis coefficient as IEC plays a significant role in the selectivity of ions [10,13]. The linkage of cationic head group groups to the polymer architecture can result in lower selectivity between proton (H^+) and other cations. Further, the AEMs with higher IEC exhibit excessive swelling degree and modest mechanical stability. Many polymer backbones such as polysulfone [14], poly(tetrafluoroethylene) [15], polyvinyl alcohol (PVA) [16], chitosan [17], polybenzimidazole [18], and bromo-methylated poly(phenylene oxide) (BPPO) [19–21], etc., were employed for the fabrication of AEMs. Because of excellent mechanical properties and membrane forming ability, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is largely employed as polymer backbone for AEMs. Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) was obtained via bromination reaction of PPO that acts as a precursor for anionic exchange. The use of BPPO for membrane synthesis as polymer architecture will remove the use of toxic material such as chloromethyl ether (CME) [22]. BPPO possess an excellent hydrolytic stability, high class of transition temperature, and high mechanical stability [23]. It exhibits excellent formation and functionalizable properties due to existence of highly reactive $–CH_2Br$ group [24].

On the other hand, the cationic head groups of AEMs were also analyzed. They are also important and decide the anion permeability of AEMs. A good cationic head group should have cheap starting material, simple fabrication procedure, and higher anion permeability. Several AEMs were synthesized containing cationic head group such as guanidinium [25–28], sulfonium [29], and phosphonium [30–34]. These membranes showed excellent anion permeability but their starting material was costly and synthetic method was difficult. To overcome this issue, we will use a new functional group for the synthesis of AEMs, which were derived from 4-(dimethylamino)butyraldehyde diethyl acetal (DABDA). The DABDA based cation contains a long substituent with two ether-containing branches, which will enhance the hydrophilicity of the substituent and useful for ion transport across the membranes. Therefore, the presence of two ether moieties into DABDA cation is advantageous for the higher transport of ions across the membrane.

In this manuscript, a series of homogeneous AEMs with different physico-chemical properties were prepared by changing amount of ion exchange moiety into the membrane matrix via the solution casting method. They were characterized physico-chemically in detail. The acid recovery performance of prepared AEMs was evaluated via diffusion dialysis process at 25°C. Moreover, the effect of temperature on diffusion dialysis performance of AEMs was also revealed in detail.

2. Experimental

2.1. Materials

Poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) was kindly supplied by Sigma-Aldrich chemicals (Germany). Chlorobenzene, ethanol, chloroform, 2,2′-azo-bis-isobutyro nitrile (AIBN), *N*-bromo-succinimide (NBS), *N*-methyl-2-pyrrolidone (NMP), 4-(dimethylamino) butyraldehyde diethyl acetal (DABDA), sodium chloride (NaCl), silver nitrate ($AgNO_3$), sodium sulfate (Na_2SO_4), potassium chromate (K_2CrO_4), hydrochloric acid (HCl), ferrous chloride ($FeCl_2·4H_2O$), methyl orange (MO) were kindly provided by Sinopharm Chemical Reagent Co., Ltd., China and employed as recieved. Deionized water was used throughout this work.

2.2. Bromination of poly(2,6-dimethyl-1,4-phenyleneoxide)

Bromination of poly(2,6-dimethyl-1,4-phenyleneoxide) (PPO) was carried according to the previously reported procedure [35]. In a typical method, 6 g of PPO (50 mmol) was dissolved into chlorobenzene (50 mL) in a round bottom flask containing a magnetic stirrer and reflexed condenser. NBS (4.45 g, 25 mmol), and AIBN (0.25 g, 1.5 mmol) were added into above stirred solution of PPO. The mixture was heated at 135°C for 3 h. After cooling at room temperature, the reaction mixture was poured into excess of ethanol to precipitate the product. The polymer was filtered and washed with ethanol, and the residue subsequently re-dissolved into chloroform (60 mL) and precipitated into an excess of ethanol solution. The polymer was collected as a light-yellow powder and dried under vacuum for 2 d at 40°C.

2.3. Preparation of AEM by solution casting method

In this work, a series of homogeneous AEMs were fabricated by using solution casting method. Initially 0.7 g of brominated poly (2,6-dimethyl-1,4-phenyleneoxide) (BPPO) was dissolved into *N*-methyl-2-pyrrolidone to form 7% (w%) solution. A series of AEMs with different physico-chemical properties were prepared by adding 0.2, 0.3, 0.35, and 0.40 g of 4-(dimethylamino)butyraldehyde diethyl acetal (DABDA) into the prepared casting solution. The prepared AEMs were named as DABDA-28, DABDA-42, DABDA-50, and DABDA-57, where 28, 42, 50, and

57 refer to the percentage of DABDA into the membrane matrix. The reaction mixture was stirred at 40°C overnight and then cast onto a glass plate at 60°C for 1 d. We peeled off the membranes from glass plates and cleaned them with distilled water. The chemical structure of the fabricated AEMs is depicted in Fig. 1.

2.4. Characterizations

2.4.1. Instrumentations

The bromination of PPO was confirmed by using ^{1}H NMR (DMX 300 NMR spectrometer operating at 300 MHZ). The attenuated total reflectance (ATR) with Fourier transform infrared (FTIR) spectrometer (Vector 22, Bruker, Kyoto, Japan) in the range of 4,000–400 cm^{-1} was employed to confirm the synthesis of AEMs. Morphology of the fabricated AEMs was revealed by field emission scanning electron microscopy (FE-SEM, Sirion200, FEI Company, USA). The thermal stability of synthesized membranes was analyzed by using a Shimadzu TGA-50H analyzer (Kyoto, Japan) with a heating rate of 10°C/min within the temperature range 25°C–800°C under nitrogen flow. Mechanical stability of wet AEMs was studied by employing Q800 dynamic mechanical analyzer (DMA, TA Instruments) at a stretch rate of 0.5 N/min.

2.4.2. Water uptake, linear swelling ratio, and IEC

Water uptake of the prepared membranes was measured by immersing accurately weighted dried membrane samples into deionized water at 25°C. The wet weight of the membranes was determined after removing surface water with tissue paper. It was measured from the difference in mass before and after drying of the membranes by the following equation [10]:

$$W_R = \frac{W_{WET} - W_{DRY}}{W_{DRY}} \times 100\% \tag{1}$$

where W_{WET} and W_{DRY} represent respectively the wet and dry weights of AEMs.

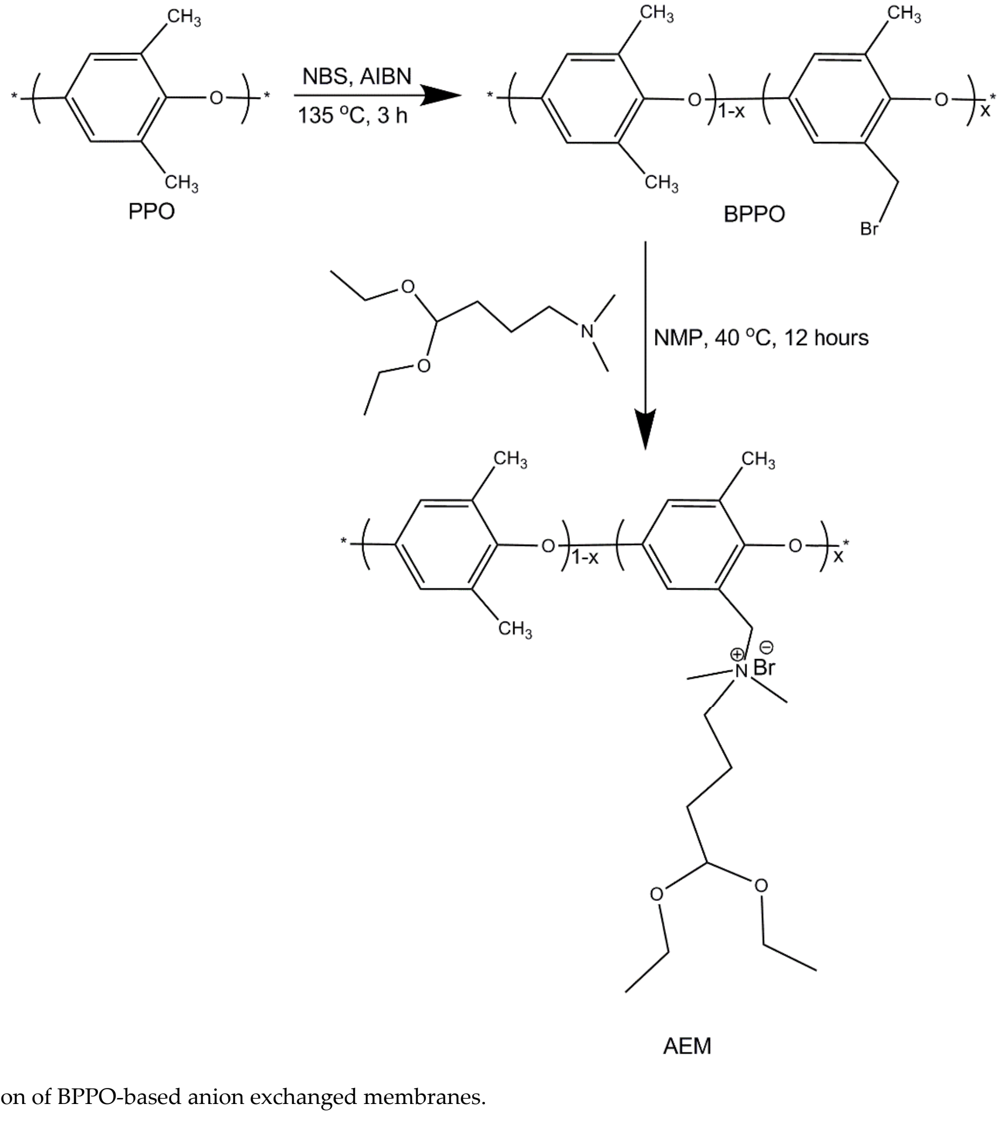

Fig. 1. Preparation of BPPO-based anion exchanged membranes.

For the prepared membranes, the linear swelling ratio (LSR) was investigated at room temperature. In order to determine it, the membranes sample was cut into (3 × 3) cm^2 pieces. It was calculated from the below equation [36]:

$$\text{LER} = \frac{\left(L_{\text{WET}} - L_{\text{DRY}}\right)}{L_{\text{DRY}}} \times 100\% \tag{2}$$

In Eq. (2), L_{WET} and L_{DRY} depict wet and dry lengths membrane samples, respectively.

The most reported method in literature such as classical Mohr's method was used to measure IEC of the prepared AEMs [11,12,20,37,38]. Initially, dried membrane samples were soaked into 1.0 M NaCl solution for 2 d such that all the charge sites were converted into the Cl$^-$ form. The membranes samples were washed with deionized water to eliminate excessive NaCl, and then soaked in 0.5 M Na_2SO_4 solution for 2 d. The amount of Cl$^-$ ions liberated was measured by titration with 0.05 M $AgNO_3$ by employing K_2CrO_4 as an indicator. It was determined by the following equation:

$$\text{IEC} = \frac{C_{\text{AgNO}_3} V_{\text{AgNO}_3}}{W_{\text{Dry}}} \tag{3}$$

where m, V, and C, respectively, represent the dry weight of the membrane sample, titer volume during titration, and the concentration of $AgNO_3$ solution.

2.4.3. Chemical stability of membranes

The chemical stability of the prepared membrane was revealed by soaking into HCl/$FeCl_2$ feed solution at 60°C. The chemical stability was measured from weight loss as a function of immersion time.

2.4.4. Diffusion dialysis of HCl/$FeCl_2$ mixture

Diffusion dialysis performance of the prepared AEMs was evaluated in a two-compartment stack which was separated by the membrane having an effective area of 5.7 cm^2. The membrane was conditioned in the feed solution (0.89 M HCl + 0.25 M $FeCl_2$) for 12 h and then cleaned with deionized water before employing into diffusion dialysis test. During this test, one compartment of the stack was filled up with 100 mL feed solution while the other side with 100 mL deionized water. To eliminate the concentration polarization, both side solutions were stirred equally and vigorously. Diffusion dialysis test was carried out for each membrane. Finally, both feed and permeate were removed from different compartments. The concentrations of H$^+$ on both compartments were investigated by titration method while Fe^{2+} concentration was calculated by utilizing inductive coupled plasma spectrophotometry (ICP, Optima 7300 DV).

The dialysis coefficients (U) can be calculated by using the below given formula [10,39]:

$$U = \frac{M}{At\Delta C} \tag{4}$$

In Eq. (4), M represents the amount of component transported (mol), A shows the effective membrane area (m^2) of membrane, t depicts the time (h), and ΔC shows the logarithm average concentration between the two chambers (mol/m^3). ΔC was calculated from below equation [10,39]:

$$\Delta C = \frac{C_f^0 - \left(C_f^t - C_d^t\right)}{\ln\left[C_f^0 / \left(C_f^t - C_d^t\right)\right]} \tag{5}$$

where C_f^0 and C_f^t are feed concentrations at time 0 and t, respectively, and C_d^t is the dialysate.

Dialysis coefficient U_{H} and U_{Fe} can be calculated by employing Eqs. (4) and (5). The separation factor (S) is ratio of dialysis coefficients (U) of the two species lies in the solution. It can be determined from the below equation [10,39]:

$$S = \frac{U_{\text{H}}}{U_{\text{Fe}}} \tag{6}$$

3. Results and discussion

3.1. Preparation of brominated poly(2,6-dimethyl-1, 4-phenyleneoxide)

Bromination of PPO was achieved successfully by using NBS as a brominating agent and AIBN as an initiator. Bromination can occur either at benzylic position or at the aromatic ring depending on the reaction condition and reagents [35,40]. In the present work, it occurred at the benzylic position of PPO in refluxing chlorobenzene solution at 135°C employing the above discussed conditions. ^{1}H NMR spectroscopy was used to investigate the structure and degree of bromination of BPPO and attained ^{1}H NMR spectrum is depicted in Fig. 2. ^{1}H NMR spectrum of BPPO shows that the characteristic benzyl bromide group was present at 4.3 ppm. The degree of bromination was 75% measured from the integral area ratio between benzyl bromide group and unreacted benzyl signal at 2.1 ppm.

3.2. FTIR test of prepared AEMs

The successful fabrication of AEMs was confirmed via FTIR spectroscopy. The FTIR spectrum of pure BPPO as well as the fabricated membrane DABDA-57 is denoted in Fig. 3. The bands at 1,446 cm^{-1} are because of stretching of –CH groups (V and δ) [41]. The band at 1,608 cm^{-1} is due to C=C stretching vibration in phenyl groups; the peak at 1,190 cm^{-1} is the characteristic of C–O–C stretching [42]. The adsorption peaks of symmetrical and asymmetrical stretching vibration of C–O are at 1,200 and 1,306 cm^{-1} and those of phenyl group at 1,470 and 1,600 cm^{-1}, respectively [36]. The characteristic band at 1,080 cm^{-1} observed in the fabricated membrane DABDA-57 was due to C–N stretching vibration. This band was absent in the spectra of the pure BPPO membrane. It represents the successful quaternization of BPPO with DABDA. The band at 750 cm^{-1} for C-Br stretching in pure BPPO disappeared after quaternization of BPPO with DABDA [43,44]. The broadband at

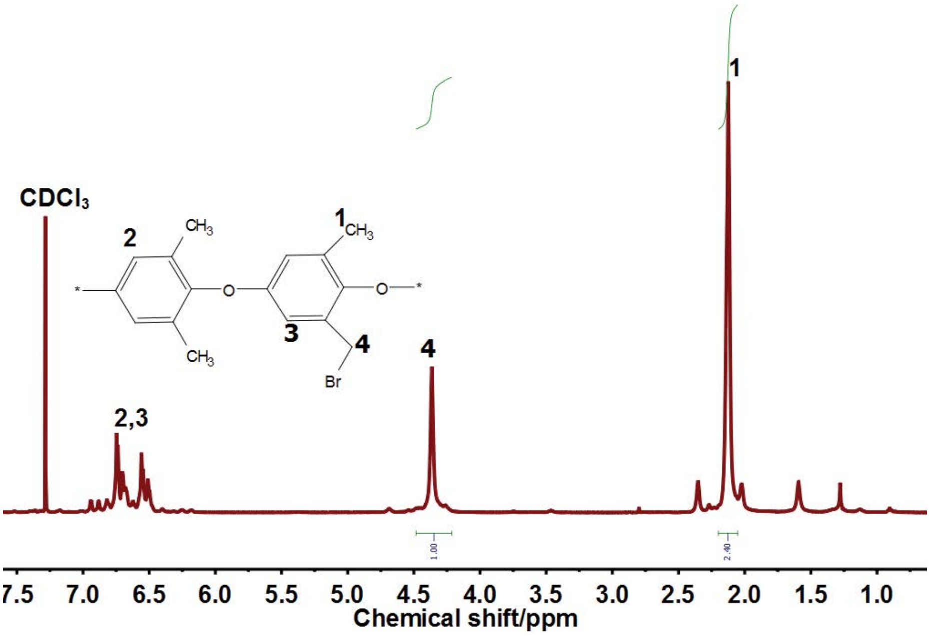

Fig. 2. ^{1}H NMR spectra of BPPO.

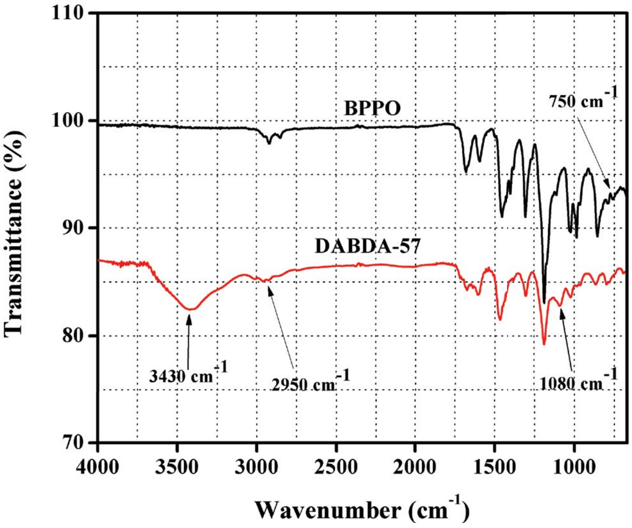

Fig. 3. IR spectrum of pristine BPPO and DABDA-57 membranes.

3,430 cm^{-1} is associated with stretching vibrations of the hydrogen-bonded –OH group in water molecules, which was absorbed during the FTIR testing because of the hydrophilicity of the prepared membrane [45]. Moreover, the band at 2,940 cm^{-1} for $-CH_3$ group becomes broad in the area due to linkage of methyl group-containing DABDA to the BPPO architecture via quaternization reaction. It proves successful preparation of the AEMs.

3.3. Thermal and mechanical stability

Thermal stability of the prepared AEMs as well as pristine BPPO membranes were revealed within the temperature range of 30°C–700°C via thermogravimetric analysis and attained results are represented in Fig. 4. It has been observed that the weight loss of the studied membranes was achieved in three stages. The first weight loss stage was found around 80°C–140°C which is associated with the evaporation of surface adsorbed water from the membrane. The weight loss in the range of 180°C–250°C was due to the degradation of the quaternary ammonium group inside the membrane matrix [10,36]. The final weight loss observed around 450°C corresponds to the degradation of the polymer backbone. This study revealed that the prepared AEMs exhibited good thermal stability.

Mechanical stability of the developed AEMs was revealed by utilizing DMA in the wet state. Table 1 shows tensile strength (TS) and elongation at break (E_b) of the fabricated AEMs at room temperature. For the prepared AEMs, the elongation at break was found to be increased whereas tensile strength was found to be decreased with increasing ion-exchange content into the polymer matrix. From Table 1, it can be seen that DABDA-28 showed higher tensile strength but lower elongation at break. On the other hand, DABDA-57 represented lower tensile strength and higher elongation at break. From this, we concluded that the developed AEMs showed higher mechanical stability.

3.4. Water uptake, IEC, and LSR

Water uptake of ion exchange membrane is a crucial property that should be taken into consideration for the diffusion dialysis process. It represents the water holding capacity of the ion exchange membrane. It is directly related to ion exchange moiety and hydrophilicity of the ion exchange membrane whereas hydrophilicity is based on the ion exchange content inside the membrane matrix. For the higher performance of AEMs, it must be higher. Table 2 represents the water uptake of the prepared AEMs at

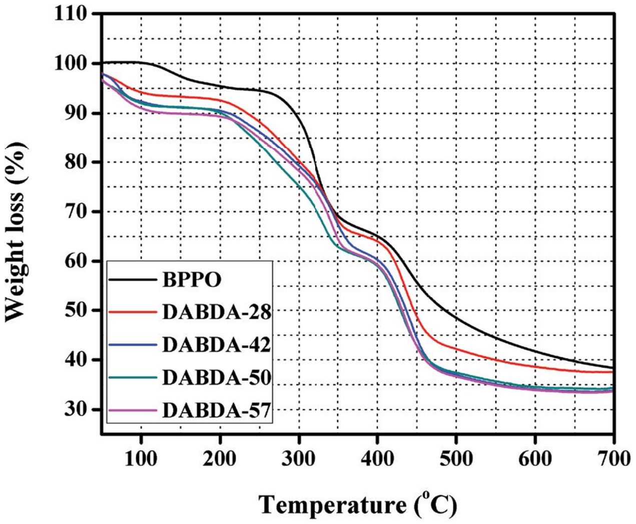

Fig. 4. TGA curves of pristine BPPO and prepared membranes.

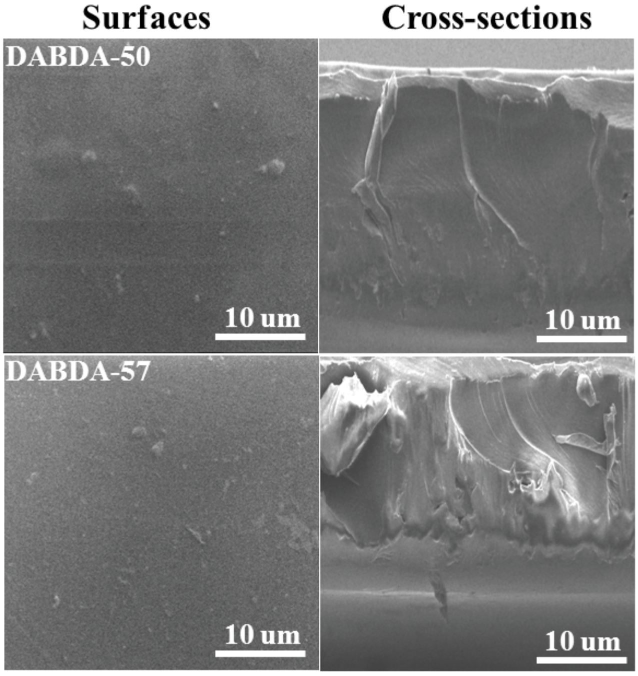

Fig. 5. SEM micrographs of surfaces and cross-sections of the prepared membranes DABDA-50 and DABDA-57 representing the homogeneous morphology.

Table 1
Tensile strength (TS) and elongation at break (E_b) of the prepared anion exchange membranes representing excellent mechanical stability

Membranes	TS (MPa)	E_b (%)
DABDA-28	64.21 ± 3.21	5.81 ± 0.29
DABDA-42	37.60 ± 1.88	8.12 ± 0.41
DABDA-50	32.74 ± 1.16	10.45 ± 0.52
DABDA-57	16.30 ± 0.82	12.0 ± 0.50

room temperature. For the prepared membranes DABDA-29 to DABDA-57, water uptake was found to 15%–36%. The water uptake was found to be enhanced from 15% to 36% with increasing the amount of ion exchange content into the membrane matrix. The water molecules support the transport of ions through the ion exchange membrane [46]. Therefore, the AEM (DABDA-57) with higher water uptake assists the transport of more ions through it.

IEC usually represents the charged nature of ion exchange membranes [47]. It is important endowment of ion exchange membranes that controls diffusion dialysis performance. Herein, the classical Mohr's method was used to measure ion exchange of the fabricated AEMs. IEC of the prepared AEMs is represented in Table 2. For the fabricated membrane DABDA-19 to DABDA-57, it was found to be 1.41–1.90 mmol/g. The amount of ion exchange content (DABDA) inside the membrane matrix is known to influence IEC of AEMs. It was found to be enhanced from 1.41 to 1.90 mmol/g with increasing amount of DABDA into the membrane matrix. The prepared AEM with lower amount of ion exchange content (DABDA-29) shows lower IEC (1.41 mmol/g) whereas the prepared AEM with higher amount of ion exchange content (DABDA-57) shows higher IEC (1.90 mmol/g).

LSR is a crucial endowment of ion exchange membranes. It was conducted to measure dimensional stability of the fabricated membrane at room temperature and attained results are shown in Table 2. For membranes DABDA-29 to DABDA-57, it was found to be 3.6%–21.4%. It has been observed that it was found to be increased from membrane DABDA-29 to DABDA-57 at room temperature. Higher concentration of DABDA leads to higher LSR and vice versa. As can be observed from Table 2, the increase in the amount of DABDA into the membrane matrix lead to increase in LSR of the prepared membranes.

Table 2
Theoretical ion exchange capacity (IEC), experimental ion exchange capacity, water uptake (W_R), and linear swelling ratio (LSR) of the prepared anionic exchange membranes at room temperature

Membranes	IEC_T (mmol/g)	$IEC_{Exp.}$ (mmol/g)	W_R (%)	LSR (%)
DABDA-28	1.17	1.42 ± 0.028	15.70 ± 0.45	3.6 ± 0.18
DABDA-42	1.59	1.47 ± 0.029	24.73 ± 0.74	6.1 ± 0.31
DABDA-50	1.76	1.73 ± 0.035	27.93 ± 0.84	15.8 ± 0.79
DABDA-57	1.92	1.97 ± 0.038	35.87 ± 1.10	21.4 ± 1.10

3.5. Morphological study

Morphology of surfaces and cross-sections of two selected AEMs such as DABDA-50 and DABDA-57 is represented in Fig. 5. Morphology of only two membranes was studied by using FE-SEM (Sirion200, FEI Company, USA) because all the prepared AEMs possess same appearance and identical fabrication conditions. The detail studies represent that increasing the amount of ion exchange content gradually into the membrane matrix leads to the homogeneous morphology of the prepared AEMs. The surfaces of both selected AEMs showed dense morphology through small roughness was also seen onto these membranes. The cross-sectional analysis showed that overall morphology is homogenous but with small roughness. The lack of holes or cracks into the studied membranes recommended their homogeneous morphology. To attain higher acid recovery of the prepared AEMs, homogeneous morphology is required. Therefore, the prepared AEMs can be used to achieve higher acid recovery via the diffusion dialysis process.

3.6. Chemical stability

Fig. 6 represents the chemical stability of the fabricated membrane DABDA-57 into HCl/$FeCl_2$ feed solution. The chemical stability was revealed in terms of weight loss by soaking the prepared membrane (DABDA-57) into HCl/$FeCl_2$ feed solution for 10 d at 60°C. The attained results exhibited that the weight loss of the studied membrane was not significant confirming its good chemical stability into feed solution. Therefore, the synthesized AEMs are excellent for acid recovery via the diffusion dialysis process.

3.7. Diffusion dialysis performance of the prepared AEMs

The acid recovery of the prepared AEMs was studied by using a mixture of HCl and $FeCl_2$ as model feed via diffusion dialysis process. The diffusion dialysis process was carried out in a two-compartment cell in batch mode at room temperature. The solution in both compartments of the cell was stirred equally and vigorously for a specific time. The diffusion dialysis coefficient of acid (U_H^+) was measured at room temperature and is depicted in Fig. 7a. For the prepared membrane DABDA-29 to DABDA-57, the diffusion coefficient of acid (U_H^+) was found to be increased from 4.5 to 28 (10^{-3} m/h) with an increasing amount of DABDA into the membrane matrix at 25°C. Compared with commercial membrane DF-120B (U_H^+ = 0.004 m/h) and QPPO/SiO_2 hybrid membranes (U_H^+ = 0.010 m/h), the obtained results were much inspiring at 25°C [2,10]. Table 3 represents an interesting comparison of the prepared AEMs with membranes reported in the literature. These results showed that the prepared membranes have excellent potential for acid recovery. The enhancement in the U_H^+ is associated with the transport of ions across the membranes. With enhancing the amount of DABDA from membranes DABDA-29 to DABDA-57, IEC of the prepared AEMs was found to be enhanced. In other words, the membrane with high IEC possesses more ionic sites. These ionic sites support the transport of ions particularly chloride ions (Cl^-) across the membranes. To fulfill the conditions of electrical neutrality, the H^+ ions may also diffuse with chloride ions because they have lower valence state [48,49]. Therefore, the concentration of H^+ was enhanced which lead to increase in U_H^+ value of the prepared membranes.

The separation factor (S) is ratio of U_H^+ to U_{Fe}^{2+}. The measured value of *S* for the prepared AEMs is represented ion Fig. 7b. The value of *S* for the fabricated membrane (BABDA-29 to DABDA-57) was in the range 178–305 at 25°C. These results showed that the value *S* for the prepared AEMs is higher than commercial membrane DF-120B [10] and previously reported membranes [50,51] at 25°C. It has been observed that the value of *S* follows a declining trend from membranes DABDA-29 to DABDA-57 with increasing the concentration of DABDA into the membrane matrix. The decrease in separation factor can be explained in the view of phase-separation morphology of the fabricated membranes at room temperature. The enhancement in the amount of DABDA into the membrane matrix from DABDA-29 to DABDA-57 results in micro-phase-separation morphology. Therefore, the chloride ion (Cl^-) and ferrous ion (Fe^{2+}) were passed free without much resistance across the membrane with H^+. This free movement of Cl^- and Fe^{2+} ions across the membrane was not good for its selectivity [52]. Hence, the separation factor of the prepared membranes DABDA-29 to DABDA-57 was decreased with increasing the amount of DABDA into the polymer matrix at 25°C.

For our best prepared AEM (DABDA-57), we also revealed the acid recovery performance via diffusion dialysis process at elevated temperature. The attained diffusion dialysis coefficient of HCl (U_H^+) of the prepared membrane DABDA-57 at elevated temperature is represented in Fig. 8a. From 25°C to 60°C, the U_H^+ for membrane DABDA-57 followed an increasing trend from 28 to 81 (10^{-3} m/s). It is associated with the enhanced transport of ions at an increased temperature [53,54]. Water uptake of membrane played a crucial role in the ion transportation at higher

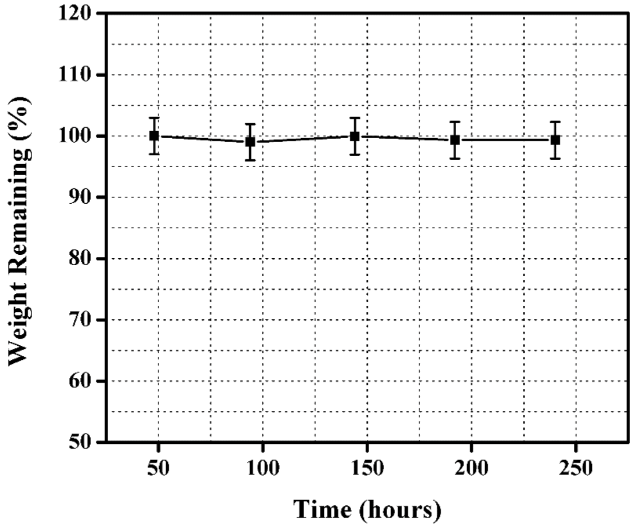

Fig. 6. Weight remaining of the prepared membrane DABDA-57 after immersion in HCl/$FeCl_2$ feed solution for 240 h at 60°C.

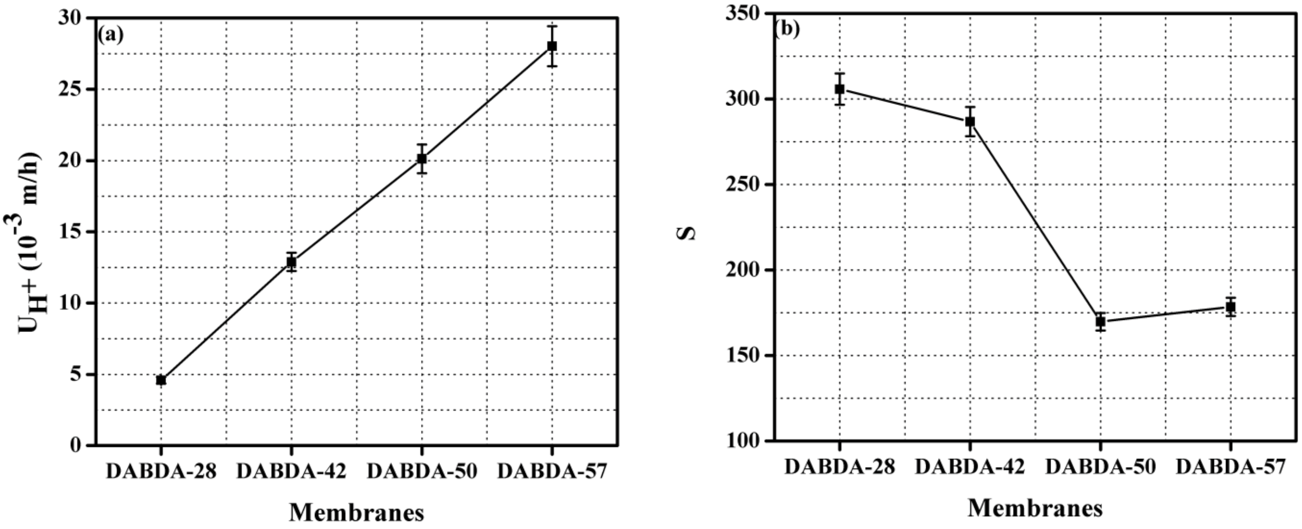

Fig. 7. (a) Diffusion dialysis coefficient of acid (U_H^+) and (b) separation factor (S) of the prepared anion exchange membranes at 25°C.

Table 3
Structure, ion exchange capacity, diffusion dialysis coefficient, and separation factor of the prepared AEMs and reported membrane employing $HCl/FeCl_2$ as the model acidic waste solution at 25°C

Membranes	Structure	IEC (mmol/g)	U_H^+ (10^{-3} m/h)	S	Ref.
DABDA based membranes	Dense	1.17–1.92	4.5–28	178–305	This work
PVA based hybrid membranes	Dense	0.58–1.15	11–18	18.5–21	[48]
PVA-silica anion exchange hybrid membranes	Dense	0.52–1.01	8–10	15.9–21	[55]
Quaternized bionic multisilicon copolymers	Dense	0.46–1.25	7.20–7.50	26.9–42.8	[56]
PVA-based anion exchange hybrid membranes	Dense	0.34–0.76	10–17	12–35	[41]
Quaternized PPO based hybrid membranes	Dense	1.70–2.20	5–11	17–32	[53]
Quaternized PPO based membranes	Dense	1.10–1.80	6–18	16–28	[19]

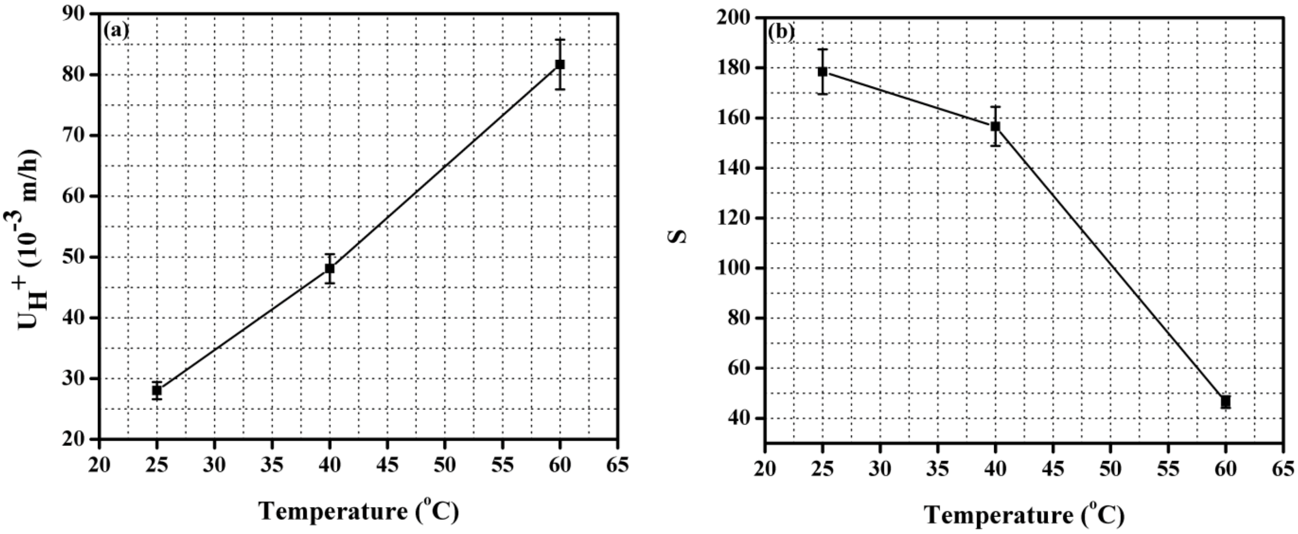

Fig. 8. (a) Diffusion dialysis coefficient of acid (U_H^+), (b) separation factor (S) of the prepared anion exchange membranes at different temperature.

temperature [50]. Within the membrane, the ions need a specific volume of water to allow their transportation when they become more hydrated. The ion with a smaller size possesses higher mobility [53]. Therefore, several H^+ were migrated at a higher temperature. Hence, the value of U_H^+ for the prepared membrane DABDA-57 was enhanced from 25°C to 60°C. Fig. 8b shows the separation factor of the prepared membrane DABDA-57 at elevated temperature. The separation factor of the prepared membrane DABDA-57 followed a descending trend from 178 to 46 with an increase in temperature from 25°C to 55°C. It was attributed to the reason that the increase in the ion transport of Fe^{2+} is more significant than H^+ at higher temperatures [53,54]. At elevated temperature, the transportation of Fe^{2+} was significant due to higher containment of water which results in to decrease in the separation factor of the prepared AEM.

4. Conclusions

In summary, the successful synthesis of homogeneous AEMs was achieved via the solution casting method. The FTIR spectroscopy confirmed the successful preparation of AEMs. The prepared AEMs exhibited homogeneous morphology. For the prepared membranes, water uptake, LSR, and IEC were increased with increasing the amount of DABDA into the membrane matrix. They showed excellent thermal, mechanical, and chemical stability. The prepared membranes showed excellent performance with higher acid recovery and selectivity compared to many previously reported membranes at room temperature. The diffusion dialysis coefficient of acid (U_H^+) was in the range of 4.5–28 (10^{-3} m/h) and the separation factor was in the range of 178–305. Moreover, the diffusion dialysis coefficient of acid (HCl) was enhanced with temperature up to 0.081 m/h at 60°C. Therefore, the performance of the prepared AEMs is excellent to be used for an acid recovery application.

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References

[1] C. Wei, X. Li, Z. Deng, G. Fan, M. Li, C. Li, Recovery of H_2SO_4 from an acid leach solution by diffusion dialysis, J. Hazard. Mater., 176 (2010) 226–230.

[2] A. Agrawal, K.K. Sahu, An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, J. Hazard. Mater., 171 (2009) 61–75.

[3] T. Xu, W. Yang, Industrial recovery of mixed acid ($HF+HNO_3$) from the titanium spent leaching solutions by diffusion dialysis with a new series of anion exchange membranes, J. Membr. Sci., 220 (2003) 89–95.

[4] J. Luo, C. Wu, T. Xu, Y. Wu, Diffusion dialysis-concept, principle and applications, J. Membr. Sci., 366 (2011) 1–16.

[5] C.-H. Shin, J.-Y. Kim, J.-Y. Kim, H.-S. Kim, H.-S. Lee, D. Mohapatra, J.-W. Ahn, J.-G. Ahn, W. Bae, Recovery of nitric acid from waste etching solution using solvent extraction, J. Hazard. Mater., 163 (2009) 729–734.

[6] J. Xu, S. Lu, D. Fu, Recovery of hydrochloric acid from the waste acid solution by diffusion dialysis, J. Hazard. Mater., 165 (2009) 832–837.

[7] N.U. Afsar, B. Erigene, M. Irfan, B. Wu, T. Xu, W. Ji, K. Emmanuel, L. Ge, T. Xu, High performance anion exchange membrane with proton transport pathways for diffusion dialysis, Sep. Purif. Technol., 193 (2018) 11–20.

[8] J.R. Varcoe, P. Atanassov, D.R. Dekel, A.M. Herring, M.A. Hickner, P.A. Kohl, A.R. Kucernak, W.E. Mustain, K. Nijmeijer, K. Scott, Anion-exchange membranes in electrochemical energy systems, Energy Environ. Sci., 7 (2014) 3135–3191.

[9] J. Ran, L. Wu, Y. Ru, M. Hu, L. Din, T. Xu, Anion exchange membranes (AEMs) based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and its derivatives, Polym. Chem., 6 (2015) 5809–5826.

[10] M.I. Khan, M. Khraisheh, F. Almomani, Fabrication and characterization of pyridinium functionalized anion exchange membranes for acid recovery, Sci. Total Environ., 686 (2019) 90–96.

[11] M.I. Khan, Comparison of different quaternary ammonium groups on desalination performance of BPPO-based anion exchange membranes, Desal. Water Treat., 108 (2018) 49–57.

[12] M.I. Khan, M. Khraisheh, Synthesis and characterization of stable anion exchange membranes for desalination applications, Desal. Water Treat., 113 (2018) 36–44.

[13] N. Li, M.D. Guiver, Ion transport by nanochannels in ion-containing aromatic copolymers, Macromolecules, 47 (2014) 2175–2198.

[14] N. Li, Q. Zhang, C. Wang, Y.M. Lee, M.D. Guiver, Phenyltrimethylammonium functionalized polysulfone anion exchange membranes, Macromolecules, 45 (2012) 2411–2419.

[15] J.R. Varcoe, R.C.T. Slade, E. Lam How Yee, S.D. Poynton, D.J. Driscoll, D.C. Apperley, Poly(ethylene-co-tetrafluoroethylene)-derived radiation-grafted anion-exchange membrane with properties specifically tailored for application in metal-cation-free alkaline polymer electrolyte fuel cells, Chem. Mater., 19 (2007) 2686–2693.

[16] K. Emmanuel, C. Cheng, B. Erigene, A.N. Mondal, M.M. Hossain, M.I. Khan, N.U. Afsar, G. Liang, L. Wu, T. Xu, Imidazolium functionalized anion exchange membrane blended with PVA for acid recovery via diffusion dialysis process, J. Membr. Sci., 497 (2016) 209–215.

[17] F. Song, Y. Fu, Y. Gao, J. Li, J. Qiao, X.-D. Zhou, Y. Liu, Novel alkaline anion-exchange membranes based on chitosan/ethenylmethylimidazoliumchloride polymer with ethenylpyrrolidone composites for low temperature polymer electrolyte fuel cells, Electrochim. Acta, 177 (2015) 137–144.

[18] N. Chen, H. Zhu, Y. Chu, R. Li, Y. Liu, F. Wang, Cobaltocenium-containing polybenzimidazole polymers for alkaline anion exchange membrane applications, Polym. Chem., 8 (2017) 1381–1392.

[19] M.I. Khan, R. Luque, P. Prinsen, A. Rehman, S. Anjum, M. Nawaz, A. Shaheen, S. Zafar, M. Mustaqeem, BPPO-based anion exchange membranes for acid recovery via diffusion dialysis, Materials, 10 (2017) 1–11, doi: 10.3390/ma10030266.

[20] M.I. Khan, R. Luque, S. Akhtar, A. Shaheen, A. Mehmood, S. Idress, S. Buzdar, A. Rehman, Design of anion exchange membranes and electrodialysis studies for water desalination, Materials, 9 (2016) 1–14, doi: 10.3390/ma9050365.

[21] M.I. Khan, A.N. Mondal, B. Tong, C. Jiang, K. Emmanuel, Z. Yang, L. Wu, T. Xu, Development of BPPO-based anion exchange membranes for electrodialysis desalination applications, Desalination, 391 (2016) 61–68.

[22] J. Zhou, M. Unlu, J.A. Vega, P.A. Kohl, Anionic polysulfone ionomers and membranes containing fluorenyl groups for anionic fuel cells, J. Power Sources, 190 (2009) 285–292.

[23] T. Xu, D. Wu, L. Wu, Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)—a versatile starting polymer for proton conductive membranes (PCMs), Prog. Polym. Sci., 33 (2008) 894–915.

[24] E. Shamsaei, Z.-X. Low, X. Lin, A. Mayahi, H. Liu, X. Zhang, J. Zhe Liu, H. Wang, Rapid synthesis of ultrathin, defect-free ZIF-8 membranes via chemical vapour modification of a polymeric support, Chem. Commun., 51 (2015) 11474–11477.

[25] Q. Zhang, S. Li, S. Zhang, A novel guanidinium grafted poly(aryl ether sulfone) for high-performance hydroxide exchange membranes, Chem. Commun., 46 (2010) 7495–7497.

[26] J. Wang, S. Li, S. Zhang, Novel hydroxide-conducting polyelectrolyte composed of an poly(arylene ether sulfone) containing pendant quaternary guanidinium groups for alkaline fuel cell applications, Macromolecules, 43 (2010) 3890–3896.

[27] L. Liu, Q. Li, J. Dai, H. Wang, B. Jin, R. Bai, A facile strategy for the synthesis of guanidinium-functionalized polymer as alkaline anion exchange membrane with improved alkaline stability, J. Membr. Sci., 453 (2014) 52–60.

[28] C. Qu, H. Zhang, F. Zhang, B. Liu, A high-performance anion exchange membrane based on bi-guanidinium bridged polysilsesquioxane for alkaline fuel cell application, J. Mater. Chem., 22 (2012) 8203–8207.

[29] B. Zhang, S. Gu, J. Wang, Y. Liu, A.M. Herring, Y. Yan, Tertiary sulfonium as a cationic functional group for hydroxide exchange membranes, RSC Adv., 2 (2012) 12683–12685.

[30] S. Gu, R. Cai, T. Luo, Z. Chen, M. Sun, Y. Liu, G. He, Y. Yan, A soluble and highly conductive ionomer for high-performance hydroxide exchange membrane fuel cells, Angew. Chem. Int. Ed., 48 (2009) 6499–6502.

[31] S. Gu, R. Cai, Y. Yan, Self-crosslinking for dimensionally stable and solvent-resistant quaternary phosphonium based hydroxide exchange membranes, Chem. Commun., 47 (2011) 2856–2858.

[32] S. Gu, J. Skovgard, Y.S. Yan, Engineering the Van der Waals interaction in cross-linking-free hydroxide exchange membranes for low swelling and high conductivity, ChemSusChem, 5 (2012) 843–848.

[33] L. Jiang, X. Lin, J. Ran, C. Li, L. Wu, T. Xu, Synthesis and properties of quaternary phosphonium-based anion exchange membrane for fuel cells, Chin. J. Chem., 30 (2012) 2241–2246.

[34] K.J. Noonan, K.M. Hugar, H.A. Kostalik IV, E.B. Lobkovsky, H.D. Abruña, G.W. Coates, Phosphonium-functionalized polyethylene: a new class of base-stable alkaline anion exchange membranes, J. Am. Chem. Soc., 134 (2012) 18161–18164.

[35] N. Li, T. Yan, Z. Li, T. Thurn-Albrecht, W.H. Binder, Comb-shaped polymers to enhance hydroxide transport in anion exchange membranes, Energy Environ. Sci., 5 (2012) 7888–7892.

[36] M.I. Khan, C. Zheng, A.N. Mondal, M.M. Hossain, B. Wu, K. Emmanuel, L. Wu, T. Xu, Preparation of anion exchange membranes from BPPO and dimethylethanolamine for electrodialysis, Desalination, 402 (2017) 10–18.

[37] M.I. Khan, A.N. Mondal, K. Emmanuel, M.M. Hossain, N.U. Afsar, L. Wu, T. Xu, Preparation of pyrrolidinium-based anion-exchange membranes for acid recovery via diffusion dialysis, Sep. Sci. Technol., 51 (2016) 1881–1890.

[38] M.I. Khan, L. Wu, M.M. Hossain, J. Pan, J. Ran, A.N. Mondal, T. Xu, Preparation of diffusion dialysis membrane for acid recovery via a phase-inversion method, Membr. Water Treat., 6 (2015) 365–378.

[39] M.I. Khan, A.N. Modal, C. Cheng, J. Pan, K. Emmanuel, L. Wu, T. Xu, Porous BPPO-based membranes modified by aromatic amine for acid recovery, Sep. Purif. Technol., 157 (2016) 27–34.

[40] T. Xu, W. Yang, Fundamental studies of a new series of anion exchange membranes: membrane preparation and characterization, J. Membr. Sci., 190 (2001) 159–166.

[41] C. Wu, Y. Wu, J. Luo, T. Xu, Y. Fu, Anion exchange hybrid membranes from PVA and multi-alkoxy silicon copolymer tailored for diffusion dialysis process, J. Membr. Sci., 356 (2010) 96–104.

[42] C. Wu, Y. Wu, M. Gong, T. Xu, New anion exchanger organic–inorganic hybrids and membranes from a copolymer of glycidylmethacrylate and -methacryloxypropyl trimethoxy silane, J. Appl. Polym. Sci., 102 (2006) 3580–3589.

[43] Y. Li, T. Xu, M. Gong, Fundamental studies of a new series of anion exchange membranes: membranes prepared from bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) and pyridine, J. Membr. Sci., 279 (2006) 200–208.

[44] C.G. Arges, L. Wang, M.-s. Jung, V. Ramani, Mechanically stable poly(arylene ether) anion exchange membranes prepared from commercially available polymers for alkaline electrochemical devices, J. Electrochem. Soc., 162 (2015) F686–F693.

[45] M.M. Hossain, L. Wu, X. Liang, Z. Yang, J. Hou, T. Xu, Anion exchange membrane crosslinked in the easiest way stands out for fuel cells, J. Power Sources, 390 (2018) 234–241.

[46] A.N. Mondal, C. Cheng, Z. Yao, J. Pan, M.M. Hossain, M.I. Khan, Z. Yang, L. Wu, T. Xu, Novel quaternized aromatic amine based hybrid PVA membranes for acid recovery, J. Membr. Sci., 490 (2015) 29–37.

[47] A.N. Mondal, C. Cheng, M.I. Khan, M.M. Hossain, K. Emmanuel, L. Ge, B. Wu, Y. He, J. Ran, X. Ge, N.U. Afsar, L. Wu, T. Xu, Improved acid recovery performance by novel poly(DMAEM-co-γ-MPS) anion exchange membrane via diffusion dialysis, J. Membr. Sci., 525 (2017) 163–174.

[48] C. Cheng, Z. Yang, J. Pan, B. Tong, T. Xu, Facile and cost effective PVA based hybrid membrane fabrication for acid recovery, Sep. Purif. Technol., 136 (2014) 250–257.

[49] C. Wang, C. Wu, Y. Wu, J. Gu, T. Xu, Polyelectrolyte complex/PVA membranes for diffusion dialysis, J. Hazard. Mater., 261 (2013) 114–122.

[50] Y. He, J. Pan, L. Wu, L. Ge, T. Xu, Facile preparation of 1,8-diazabicyclo[5.4.0]undec-7-ene based high performance anion exchange membranes for diffusion dialysis applications, J. Membr. Sci., 491 (2015) 45–52.

[51] J. Feng, J. Chen, B. Wei, S. Liao, Y. Yu, X. Li, Series-connected hexacations cross-linked anion exchange membranes for diffusion dialysis in acid recovery, J. Membr. Sci., 570–571 (2019) 120–129.

[52] C. Cheng, Z. Yang, Y. He, A.N. Mondal, E. Bakangura, T. Xu, Diffusion dialysis membranes with semi-interpenetrating network for acid recovery, J. Membr. Sci., 493 (2015) 645–653.

[53] J. Luo, C. Wu, Y. Wu, T. Xu, Diffusion dialysis of hydrochloride acid at different temperatures using PPO–SiO_2 hybrid anion exchange membranes, J. Membr. Sci., 347 (2010) 240–249.

[54] X. Lin, E. Shamsaei, B. Kong, J.Z. Liu, T. Xu, H. Wang, Fabrication of asymmetrical diffusion dialysis membranes for rapid acid recovery with high purity, J. Mater. Chem. A, 3 (2015) 24000–24007.

[55] Y. Wu, C. Wu, Y. Li, T. Xu, Y. Fu, PVA–silica anion-exchange hybrid membranes prepared through a copolymer crosslinking agent, J. Membr. Sci., 350 (2010) 322–332.

[56] Y. Wu, J. Luo, C. Wu, T. Xu, Y. Fu, Bionic multisilicon copolymers used as novel cross-linking agents for preparing anion exchange hybrid membranes, J. Phys. Chem. B, 115 (2011) 6474–6483.