Highly Charged Hierarchically Structured Porous Anion Exchange Membranes with Excellent Performance

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ABSTRACT

Fabrication of Porous Anion Exchange Membranes for ion transport and ionic selectivity has gained tremendous attention as a prospect for broad application in separation and energy conversion. In this work, we developed a novel strategy to fabricate highly charged hierarchical porous anion exchange membranes (AEM) with high performance. The membranes were prepared by coupling quaternized poly (2-dimethylaminoethanol-N-2,3-dimethylphenyl oxide) (QDAPPO) and an organosilane ionic liquid (IL). The electrostatic ionic interactions provide the porous system. When applied in acid recovery, the obtained membranes achieved a high separation factor of 86.5 with proton dialysis coefficient of 0.027 m h^{-1} at 25°C . This unique efficiency is about 4.7 times that of commercial membrane. More interestingly, the strategy presents in this work tackle the great challenge of fabricating highly charged, thinner and dimensional stable AEM.

KEYWORDS: Anion Exchange membrane, hierarchical porous, ion selectivity, ionic liquid, separation

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1. Introduction

The environmental impact of world population growth is diverse because the rapid demand of food, energy and commodities increases the expansion of industries productions which lead to environmental pollution and rapid decline of the natural resources. Major industries such as metal processing, mining, pulp and paper, paintings, agriculture, vehicles, chemical and food, and electrical power plants produce acidic wastewaters contained toxic heavy metals and detrimental chemicals[1-3]. To ensure sustainable human society development, there is an increasing global concern for the wastewaters treatment within industrial production processes.[4-6] Traditional techniques such as neutralization, crystallization, distillation, thermal decomposition and solvent extraction for wastewater treatments[7-10] focus on purification rather than recovery of resources, and therefore loss enormous amount of energy stored in wastewaters while consuming additional external energy for their operating processes. Membrane based technologies like diffusion dialysis, membrane distillation, electrodialysis, microbial desalination cell, reverse electrodialysis that recover resources and/or energy from wastewaters are more promising for wastewater treatments, sustainable and environmental friendly.[11-18] Diffusion dialysis, an attractive and commercial viable technique due to its low cost and requires minimum energy during operations[5, 19-21], was selected to investigate the performance of AEMs in this work. It is noteworthy that the major challenges of membrane based techniques for wastewater treatment and acid recovery has been the fabrication of cost-effective anion exchange membranes (AEMs) with optimum desired characteristics including high permeation, high selectivity and long-term stability.

In membrane based gradient techniques for acidic wastewater treatment, AEM should selectively allow the passage of anions across the membrane while limiting the transport of the cations and thus to successfully recover acid, the proton (H^+) should cross the AEM taking advantage of its small radii and high mobility than other cations (i.e. Fe^{2+} , Cr^{2+} , Mn^{2+}). AEMs are usually prepared by attaching cationic groups (i.e. quaternary ammonium (QA), Imidazolium (Im), phosphonium and guanidium) on polymer architectures.[22-24] Compared to their counterpart proton exchange membranes (PEM), the fabrication of high performance AEMs is more challenging because the fundamental characteristics of cationic head groups and the intrinsic

nature of anions such as low dissociation, low mobility and various shape compared to cations.[25] Firstly, tailoring microphase separated morphology is much easier in PEM than in AEM because the acidity of anionic functional groups is much higher than the basicity of cationic groups. Secondly, low mobility of anions leads to lower ionic transport and poor selectivity of AEMs.[22] A facile straight forward strategy to increase the ionic transport is via increasing the ion exchange capacity (IEC) which unfortunately is usually associated with excessive membrane swelling and compromise of mechanical properties[26]. Thirdly, flexibility of AEMs becomes low as increasing the IEC in rigid aromatic polymers backbone, especially at low humidity that can make the operation failure or maintenance difficulty.[27-30] In order to increase the ion transport and selectivity while preserving the membrane dimensional integrity, previous works attempted to fabricate AEMs with controlled microphase separated morphologies[31, 32] or crosslinking polymer chains to enhance the dimensional stability toward high IEC[28, 33-37]. Although these techniques succeed to increase the ionic transport, particularly when external electrical potential is applied for ion transport like in case of electrodialysis, the membrane mass transport is very lower for feasible application in membrane techniques based on concentration gradient like diffusion dialysis. For example, the commercial available DF-120 (a dense AEM with fiber as substrate) has a proton dialysis coefficient (U_{H^+}) of only 0.009 m h^{-1} and selectivity of 18.5 at 25 °C.

To assure the high ion and mass transport of AEMs, porous membranes have been proposed for versatile applications owing to their high surface area responsible to boost the membrane permeability.[11, 19, 38] Porous asymmetric (Ultra-filtration, UF) membranes prepared via phase inversion routes have been mostly utilized for diffusion dialysis[39, 40]. Porous asymmetric AEMs prepared through immersing brominated poly(phenylene oxide) in multisilicon copolymer solution and in tertiary amine solutions for cationic functionalization followed by sol-gel reaction exhibited an improved U_{H^+} value of $0.020\text{-}0.025 \text{ m h}^{-1}$ and a separation range from 25-45 at 25 °C.[40] Very recently, Wang et al[41, 42] reported macroporous asymmetric membrane with high U_{H^+} values prepared via phase inversion of BPPO crosslinked by N,N,-tetramethylethylenediamine (TEMED) or poly(ethyleneimine) (PEI). The TPPO-4h membrane (BPPO crosslinked by TEMED) of 1.43 meq g^{-1} exhibits a high proton dialysis coefficient of 0.043 m h^{-1} and a high separation of 73.8 at 25 °C.

Consider the obtained high U_{H^+} , the performance of these membranes were counterbalanced with the diffusion of ferrous ions (Fe^{2+}) which increased as a results of wide pores and high water uptake. Additionally, porous asymmetric (UF) membranes usually have a thick layer (ca. $>300\mu m$) responsible for weakening mass transport and sometime lead to operation difficulty. Despite that, fabrication of thin layer porous membranes is still a major challenge limiting the optimization of membrane performance.

In this work, we report a novel strategy to tailor hierarchical mesoporous AEMs (HMPA) with high performance for rapid acid recovery. HMPA takes advantage of the highly charged nanosized pores in gradient structure with a moderate thickness to simultaneously enhance the selectivity and mass transport. To prepare HMPA, poly(2,3-dimethylphenyl-N-(2-hydroxy-N,N-dimethylethanaminium chloride) or quaternized poly(2-dimethylaminoethanol-N-2,3-dimethylphenyl oxide) (QDAPPO) and 3-methyl-1-(3-(triethoxysilyl)propyl)-1H-imidazolium chloride (Ionic liquid, IL) were covalently crosslinked via sol-gel reaction followed by thermal treatment at high temperature. By contrast to reported works, hierarchical porous membranes for gas separation and responsive membranes have been recently prepared by using template method or immersing IL based membranes into ammonium solutions[43-46]. More interestingly, the strategy presents in this work tackle the great challenge of fabricating highly charged AEM with thin layer and good dimensional stability.

2. Experimental

2.1. Materials

1-(2-(dimethylamino) ethanol (DMAE) was purchased from J&K chemicals Ltd and was used without further purification. Sodium sulfates, sodium chloride, Toluene, ethylacetate, NMP, diethyl ether, were purchased from Shanghai Sino Pham Chemical Reagent Co. Ltd. (P. R. China). Bromomethylated (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) of 52 bromobenzyl ($-CH_2-Br$) was provided by Tianwei Membrane Corporation Ltd.(Shandong, P.R. China). It was purified before use by dissolving in N-methyl-2-pyrrolidone (NMP), precipitating in deionized water, and drying in $30\text{ }^{\circ}C$ vacuum oven. Diionized water was used throughout the experiments.

2.2. Synthesis of quaternized poly(2-dimethylaminoethanol-N-2,3-dimethylphenyl oxide) (QDAPPO)

1.104 g (4.2 mmol) of 1-(2-(dimethylamino) ethanol (DMAE) was all at once added to a solution of 2g (5.56 mmol) BPPO in 30mL of NMP into 50mL bottom flask. The mixture was stirred at room temperature for 16 h and then poured in toluene to precipitate the product. The precipitate was filtered, washed several times by ethylacetate and final by diethylether and then dried at 40 °C for 48 h in air circulating oven. The completed substituted polymer was confirmed by ¹H NMR as determined from integration ratio of methylene and aromatic protons.

2.3. Synthesis of 3-methyl-1-(3-(triethoxysilyl)propyl)-1H-imidazolium chloride (Ion liquid, IL)

IL was prepared by following the method reported elsewhere[47] and described as follows. 1-Methylimidazole (2.060 g, 25.085 mmol) and (3-chloropropyl) triethoxysilane (6.042 g, 25.091 mmol) dissolved in toluene (20 mL) were refluxed for three days. Immediately after stop stirring and heating, viscous oil decant at the bottom of flask and then the toluene can easily removed by pouring. The obtained viscous oil was washed several times by toluene and diethylether anydrous to remove unreacted reagents. The solvents were completely removed under reduced pressure and drying for 24 h at 60 °C to afford the title product as viscous oil. The IL is soluble in other polar solvent (i.e.DMSO, Acetonitrile). The chemical structure was confirmed by ¹H and ¹³C NMR (see Figure S1 and S2, ESI)

2.4. Membrane preparation

1 g of polymer (QDAPPO) was dissolved in 10 mL of DMSO. Appropriate amount of IL (10%, 20%, 30% and 40% wt of QDAPPO) was added to the polymer solution at room temperature and allow to mixture for 30 minutes prior to subsequently add TEOS (1:1 ratio corresponding to loaded IL) and 2-3 drop of 1M HCl in DMSO. The above mixture was stirred at 45 °C for 24 h, casted on glass plate and dried at 60 °C for 12 h to remove the solvent. The membrane was peered off the glass plate and thermally treated from 70, 90, 110 and 120 °C (1h at each temperature) and at 130 °C for 3h to assure the complete sol-gel reaction and remove of tapped solvent. The obtained thermal treated membrane was immersed in water for 24 h and then in 2 M

NaCl to convert the Br⁻ ions into Cl⁻ ions. The membranes were noted as QDA-IL_x where x presents the percentage ratio of IL and TEOS to QDAPPO.

Scheme 1: Preparation of routes for QDA-IL membranes

2.5. Polymer and Membrane characterization

Nuclear Magnetic resonance (NMR) spectra were recorded on a Bruker AVANCEII spectrometer with TMS as an internal standard. Scanning electron microscopy (SEM) images were observed by using scanning electron microscopy (XT30ESEM-TM-PHILIP). The samples for SEM (for cross-sectional) were prepared by freezing and breaking samples in nitrogen liquid whereas the sample for surface imaging were prepared by directly cutting a clean membrane into small pieces. Thermal behavior was carried out on NETZSCH STA 449F3 thermogravimetric analyzer (TGA). Samples, pre-dried in vacuum oven at 60 °C for 24 h, were heated from 50 to 800 °C at a heating rate of 10°C /min under a nitrogen flow. Tensile measurements of membranes were carried out using a dynamic mechanical analyzer (DMA Q800) in controlled force mode using a stretch rate of 0.50 N/min at room temperature. Stress-strain curves were

recorded. Wet state mean that the samples were kept in water prior to testing whereas dry state mean that the samples were dried in vacuum oven before the testing to remove any trace of water.

Ion exchange capacity, Water uptake and swelling ratio were characterized in the same way as our published papers[48].

Diffusion dialysis tests were performed in a cell of two chambers where are separated by an AEM with an effective area of 5.73 cm². Assimilated acid wastewater solution filled in feed chamber at 100mL volume contains 1 mol L⁻¹ of HCl and 0.2 mol L⁻¹ of FeCl₂ mixed solution. The permeate chamber was filled with distilled water at 100mL. Prior to the test, the AEMs were conditioned in feed solution for 24 h and washed thoroughly with water before each test. Mechanical electrical stirrers were used to stir both chambers synchronously and identically to minimize concentration polarization effects. After 45min of diffusion, HCl concentration diffused in permeate solution were determined by using standard titration method with Na₂CO₃ solution using methyl orange as the indicator. The concentration of FeCl₂ was measured by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Dialysis coefficient can be calculated from the concentration of species by the following equation:

$$U = \frac{M}{At\Delta C} \quad (1)$$

Where M is the amount of the component transported in moles, A is the effective area in square meters; t is the time in h, and ΔC is the logarithmic average concentration between the two chambers in mole per cubic meter as in equation below:

$$\Delta C = \frac{(C_f^0 - C_d^t - C_f^t)}{\ln[(C_f^0 - C_d^t)/C_f^t]} \quad (2)$$

Where C_f^0 and C_f^t are the feed concentrations at time 0 and t, respectively, and C_d^t the dialysate concentration at time t. It should be noted that $(C_f^0 - C_d^t - C_f^t)$ is not equal

to zero, because water transporting through the membrane will cause volume changes in the cell chambers during the experiment.

The separation factor (S) between HCl and FeCl_2 is defined as a ratio of the dialysis coefficients of protons (U_{H^+}) and of cationic iron ($U_{\text{Fe}^{2+}}$).

$$S = \frac{U_{\text{H}^+}}{U_{\text{Fe}^{2+}}} \quad (3)$$

3. Results and Discussions

3.1 Synthesis and characterization of QDA-IL AEMs

Scheme 1 displays the preparation route of DA-IL AEMs. First, the QDAPPO was synthesized through reacting BPPO with 1-(2-(dimethylamino)ethanol) (DMAE). The initial molecular weight of BPPO was maintained throughout the synthesis since the reaction was carried at room temperature and in mild medium. After purification, the polymer structure was confirmed by the ^1H NMR and FTIR spectroscopy as shown in Figure 1 and Figure S3 (ESI). The proton characteristic peak at 4.34 ppm assigned to brominated methylene of BPPO was used to monitor the substitution reaction and determine the grafting degree. As clearly shown in Figure 1, the substituted methylene proton peaks shift to 4.5 ppm which indicates the successful reaction of BPPO with DMAE. The absence of any proton signals around 4.34 ppm suggests the fully substituted brominated methylene. The substitution degree was calculated as the ratio of the integration of the peak at 4.5 ppm and the peaks at 7-6.5 ppm. Further, the QDAPPO is confirmed by the proton characteristics peaks of $\text{N-CH}_2\text{-CH}_2\text{-OH}$; the methylene protons of $\text{-N-CH}_2\text{-}$ and $\text{-CH}_2\text{-OH}$ signal at 3.5 ppm and 3.9 ppm, respectively. Hydroxyl groups (-C-OH) are absolutely confirmed by the proton signal at 5.94 ppm. It is worth to note here that the QDAPPO has versatile solubility in several conventional solvents for membrane preparation (i.e. DMSO, Methanol, and DMF). The FTIR spectrum of QDAPPO is shown in Figure S3. The characteristics absorption bands of the QDAPPO apparently appear at $3500\text{-}3000\text{ cm}^{-1}$ (broad band, hydrogen bonding among -OH groups) and $1092\text{-}1088\text{ cm}^{-1}$ (symmetric stretching of C-N). While the disappearance of the BPPO characteristics band in finger-print region at $738\text{-}735\text{ cm}^{-1}$ corresponding to $\text{-CH}_2\text{Br}$ confirms a complete substitution reaction.

Figure 1: a) ^1H NMR spectra of BPPO (in CDCl_3) and QDAPPO (in DMSO-d_6)

Figure 2: FTIR spectra of QDAPPO and QDA-IL membranes; a) $4000\text{--}2500\text{ cm}^{-1}$ and b) $1800\text{--}600\text{ cm}^{-1}$.

DA-IL AEMs were prepared by grafting the QDAPPO and IL through sol-gel reaction. The successful completion of sol-gel reaction was monitored by the FTIR spectroscopy (Figure 2a-b). The absorption bands at 2962-2849 cm^{-1} , characteristics of methyl and methylene, become stronger than those of QDAPPO due to incorporation of IL bearing $-\text{CH}_2-$ and $-\text{CH}_3$. The absorption bands at 1086 cm^{-1} rise in intensity and become wider because the anti-symmetric stretching of Si-O-C and Si-O-Si bond while the band at 798 cm^{-1} indicates the vibration of $\nu\text{Si-O-Si}$. [49, 50]. The absorption band at 1260 cm^{-1} appears in QDA-IL membranes arise from the stretching vibration of C-N in imidazolium cation ring and the absorption band at 753 cm^{-1} confirms the vibration mode of imidazolium cations. [30] The broad band at 3500-3000 cm^{-1} are assigned to hydrogen bond among unreacted Si-OH and trace of water in the QDA-IL membranes are weakened relative to QDAPPO because most of the C-OH groups were reacted.

3.2 Membrane Morphology

The morphologies of the membranes were observed by scanning electron microscopy (SEM). As illustrated in Figure 3, interconnected three-dimensional porous structures were formed. The cross-sectional SEM images shows hierarchically distributed nanopores along the cross-sectional of the membrane. It is apparent that the QDA-IL membranes possess nanoporous structure for which the pores density and dimensions increase with increasing the IL contents. SEM images of QDA-IL1 to QDA-IL6 membranes captured on both the surface and cross-sectional are illustrated in Figure S4 and S5 (Supporting information). All QDA-IL membranes show porous structure except QDA-IL1 membrane which shows a compact surface. Membranes with different thicknesses (43-59.9 μm) were obtained due to variation of concentrations of casted solutions. The segregation of imidazolium cationic groups and their electrostatic ionic complexation with alkoxides formed during silica particles formation provided the hierarchical porous system. Consequently, the pores are cationic charged by imidazolium groups that would influence the selectivity of the membranes. Recently, a number of reported work revealed similar hierarchical pores formation when the IL complexes with anions [43, 44] via immersing partial dried membranes into anion solutions. In contrast to asymmetrical porous membranes prepared through phase inversion method, whose cross-sectional pores consists of macroporous and thick layer, the hierarchical porous structure having well-defined

interconnected pores across the membrane and low thickness can increase the tortuosity of ion transfer to improve the selectivity of the membranes and as well enhance the mass transport

Figure 3: SEM images of QDA-IL members; QDA-IL2 (a-c) and QDA-IL6 (d-e)

3.3 Ion Exchange Capacity

IEC is a primary parameter to consider for preparing and characterizing the AEMs since the transport of anions across the membranes relies mostly on the IEC due to the low mobility of anions. In this work, the IECs of QDA-IL membranes were optimized through increasing the density of cationic functional groups; quaternary ammonium from QDAPPO and imidazolium from IL. The theoretical and experimental IECs are shown in Table 1. The difference between the theoretical and experiments is attributed to the low mobility of Cl^- ion and its slow exchanging with the sulphate ions during the IEC measurement. Compared to the QDAPPO membrane, the IECs of DA-IL membranes increased significantly with addition of the IL and attain an experimental high value of 2.49 mmol g^{-1} at 25°C . The low IEC of QDA-IL1 is

attributed to reduced membrane flexibility caused by crosslinking between hydroxyl groups of polymer and silane (C-OH and Si-OH).

Table 1: Membrane composition, thickness, ion exchange capacity (IEC) and water uptake (WU)

Membrane	IL+TEOS to -OH (%)	Thickness (μm)		IEC (meq/g)		WU (%)	
		Dry ^a	Wet	IEC ^b	IEC ^c	25°C	60°C
QDAPPO	0	55.7	66.2	2.13	2.11	63.76	69.1
QDA-IL-1	10	55.1	63	2.37	2.13	51.25	52.7
QDA-IL-2	20	43.3	76	2.47	2.20	66.2	72.8
QDA-IL-3	40	56.6	81	2.55	2.24	83.92	88.0
QDA-IL-4	60	53.6	92.8	2.70	2.38	130.8	135.2
QDA-IL-5	80	59.9	101	2.83	2.42	141.1	147.6
QDA-IL-6	100	59.6	107	2.93	2.49	157.9	163.3

^aDetermined from SEM imaging, ^bTheoretical IEC, ^cExperimental IEC determine by using titration method,

3.4 Water Uptake (WU)

The Water uptake (WU) has a profound effect on the transport behavior of ions across the membrane and as well on dimensional and mechanical stability. Rationally, the high WU of the ion exchange membrane would be associated with high ion transport except that it usually undermines the selectivity of the membranes. The DA-IL membranes have the water uptake ranging from 51.25 to 157.92 % at 25 °C (Table 1). This range is reasonably viable for the DD and several other AEMs based applications. To emphasize, the WU of QDA-IL membranes are interestingly lower than that of asymmetrical porous BPPO modified TEMED[41] (ca. 330 %). The cationic groups from IL, silica particles and free volume in pores contributed on increasing the WU of QDA-IL membranes. Thermal annealing having initiated covalent crosslinking (Si-O-C) among silica and hydroxyl groups of QDAPPO decreased the membrane flexibility and consequently diminishes the WU of QDA-IL1 despite an observed slight increase on IEC. To test the swelling behavior, the DA-IL membranes were immersed in water and heated at 65 °C for 24 h. Hence, The WU increased as increasing the contents of IL. As shown in Table.1, the water uptake increases slightly as the temperature increases from 25 °C to 65 °C while all membranes maintained the initial dimensional

stability. Usually, the WU value of AEM increases with temperature as a result of increased polymer chain flexibility which frees the cationic groups to fully adsorb the water molecules.

3.5 Diffusion dialysis performance

QDA-IL membranes were used in DD to evaluate their performance for application in inorganic acid recovery. The model acidic wastewater solution used in this work contains the mixture of aqueous HCl and FeCl₂. [41, 51] This wastewater solution was preferably chosen because the Cl⁻ and Fe²⁺ ions are not only abundant in wastewaters but the Fe²⁺ ion has also a small ionic radius among the metal pollutants. Therefore, the effective performance of the AEMs in the above model solution would suggest certainly their performance in several other applications such as DD power, MDC and RED, etc.

Figure 4: Proton dialysis coefficient (U_H) and separation factor (S) of QDAPPO and QDA-IL membranes at 25 °C

Figure 5: Ferrous ion dialysis coefficient ($U_{Fe^{2+}}$) of QDAPPO and QDA-IL membranes at 25 °C

Figure 4 shows the proton dialysis coefficient (U_{H^+}) and separation factor (S) of QDA-IL and QDAPPO membranes at 25 °C. The U_{H^+} values of QDA-IL membranes are in the range of 0.020-0.0273 m h^{-1} at 25 °C except for QDA-IL1 which exhibits low U_{H^+} value of 0.0098 m h^{-1} while the U_{H^+} value of QDAPPO is 0.011 m h^{-1} at the same conditions. Compared to some reported AEMs, U_{H^+} values of QDA-IL membranes are about 3 times the value of commercial DF-120 (0.009 m h^{-1} at 25 °C) and quaternized PPO-SiO₂ membranes[52] (0.005-0.011 m h^{-1} at 25 °C), and 2 times higher than the PVA and multi-alkoxy-silicon copolymer blending membranes[48, 53] (0.01-0.017 m h^{-1} at 25 °C). The U_{H^+} trend in QDA-IL membranes first decreases with addition of 10% of the IL and then increases upon adding 20% of IL. Compared to QDAPPO, the high U_{H^+} values of QDA-IL2 to QDA-IL6 membranes are attributed to different membrane morphological structure (dense vs. hierarchical porous), different mechanical properties (rigidity vs. elasticity) and chemical compositions (crosslinked -C-OH groups vs Si-O-Si bonds). Free hydroxyl groups can easily form the hydrogen bond with proton which can accelerate the transport of HCl across the membrane whereas crosslinked -OH groups make the membrane rigid and tough. When only 10% of the IL was added, a certain amount of hydroxyl groups of QDAPPO were consumed into sol-gel reactions and through thermal annealing the unreacted hydroxyl groups undergo thermal crosslinking to form a rigid dense membrane. As a result, unreacted hydroxyl groups in QDA-IL1 lack sufficient flexibility to facilitate the diffusion of protons at 25 °C as evidenced from the DMA result (Figure 8). Upon

adding 20 % of IL, the hierarchical porous system was formed and the Si-O-Si bond increased into the membrane matrix. This contributed to the high U_{H^+} value of QDA-IL2 membrane. Despite the increase of WU with increasing the IL content, there is a decreasing trend in U_{H^+} values observed from QDA-IL2 to QDA-IL6. This trend is explained by: i) the increase of cationic groups reduce the proton diffusion because the increased friction and electrostatic repulsion[54, 55] ii) Addition of IL is marked with increase of silica particles which significantly facilitate the protons adsorption rather than desorption as a results of increased bound water.[56] iii) the competition between H^+ and Fe^{2+} ions transport in the membranes as the pore size increases since the Fe^{2+} ion has large radii and higher valence state than H^+ ion as previously reported[48]. Consequently, the U_{H^+} value decreases consistently from the QDA-IL2 to QDA-IL6. Meanwhile, as shown in Figure 5, the $U_{Fe^{2+}}$ value increases progressively with increasing the IL content as a result of increased WU and pores density. This result is in accord with general trend of $U_{Fe^{2+}}$ variation with WU. Further comparison with some reported AEMs, shows that the $U_{Fe^{2+}}$ of QDA-IL2 is about 2.2, 1.8-6 and 1.5 times the $U_{Fe^{2+}}$ value of porous asymmetrical BPPO modified by multisilicon membrane[40] ($0.000699 \text{ m h}^{-1}$), porous asymmetrical membrane BPPO modified by various amines[41, 42] ($0.000582\text{-}0.002 \text{ m h}^{-1}$) and commercial DF-120 ($0.000486 \text{ m h}^{-1}$), respectively. The decrease of $U_{Fe^{2+}}$ value from QDA-IL5 to QDA-IL6 is attributed to increase of charge density inside the pores. At first, the $U_{Fe^{2+}}$ value increases progressively as a result of increasing pores density and dimension in QDA-IL membranes. The addition of the IL in QDA-IL membranes would possibly reach a threshold of pores density and dimensions and therefore further addition of IL would alternatively increase more the pores charge density. Since the Fe^{2+} ion transport is defined mainly by the adsorption rather than diffusion, the charge density inside the pores would greatly impact the cations transport despite the increase of WU. It is essential to emphasize here that WU in QDA-IL membranes is defined by the cationic groups and bound water associated with adsorption of hygroscopic silica particles. The bound water in silica particles would have a trivial effect on the $U_{Fe^{2+}}$ value because the Fe^{2+} ion is large in size to traverse the interstitial of silica particles. The QDAPPO and QDA-IL1 exhibit the lowest $U_{Fe^{2+}}$ values of $0.000076 \text{ m h}^{-1}$ and $0.000074 \text{ m h}^{-1}$ which are attributed to compactness of the membranes initiated from crosslinking among hydroxyl groups after heat treatment. This indicates that the water

molecules are mainly bound on cationic groups which selectively allow the passage of anions (i.e. Cl^-). As a result of diffusion coefficients, the QDAPPO records the highest separation factor (S) of 145.78 which decreases upon addition of IL. From QDA-IL2 to QDA-IL6, the S decreases from 86.51 to 38.8, respectively. Despite its highest S, the mass transfer of QDAPPO is very low as indicated with the U_{H^+} values. By contrast, the QDA-IL2 to QDA-IL6 exhibit viable and high mass transfer for acid recovery. Compared to some reported AEMs for acid recovery using HCl and FeCl_2 as model acidic wastewater solution, the hierarchical porous QDA-IL2 and QDA-IL3 membranes have excellent selectivity and superior S. For example, as shown in Fig.6, the QDA-IL2 exhibits an S of 86.5 at 25 °C which is about 9.6 times the S of commercial DF-120, suggesting the ultra-selectivity of QDA-IL membranes for acid recovery.

Figure 6: Proton dialysis coefficient (U_{H^+}) of QDA-IL2 membrane at different temperature

QDA-IL2 was used to investigate the performance of diffusion dialysis at different temperatures. The results of proton diffusion coefficients and separation factor (S) are shown in Figure 6. The U_{H^+} of QDA-IL2 increases from 0.027 to 0.045 m h^{-1} with increasing temperature from 25 to 55 °C. This is attributed to the increase of protons mobility with temperature. Concurrently, its separation factor slightly increases from 86.5 to 94.7 when increases temperature from 25 °C to 55 °C, respectively. Hence, further increase of temperature to 65°C drops slightly the separation factor to 93.2. Despite the gradually increase of U_{H^+} with temperature, the high temperature increases the water mobility which facilitates as well more significantly the diffusion

of Fe^{2+} ions across the membrane. Given that the diffusion dialysis mostly performs at ambient temperature, the QDA-IL2 is an excellent choice for acid recovery.

3.6 Thermal stability

The thermal stability of the QDAPPO and QDA-IL membranes were evaluated by TGA under a nitrogen atmosphere. Obviously, the incorporation of IL enhances the thermal stability of QDA-IL membranes. From Figure 7a, the first decomposition started from low temperature (ca. 50-120 °C) is attributed to the removal of bounding water molecules in the membrane. This decomposition is much more significant for the QDAPPO membrane. The second weight loss onset at 178 °C for the QDA-IL membranes and at 141 °C for QDAPPO membrane is attributed thermal decomposition of quaternized amines. As clearly shown in Figure 7b, the derivative degradation weights of QDAPPO shows a peak at 176 °C indicating the maximum decomposition of quaternary amines whereas the QDA-IL membranes, combining both quaternary amines and imidazolium cations, exhibit maximum cationic group decompositions at 234 °C. Further comparing the QDA-IL membranes, the peak at 234 °C increases in intensity as increasing the IL content and rather shifts to high temperature for QDA-IL5 and QDA-IL6 membranes due to higher thermal stability of the imidazolium cations than the quaternary amines.[57] The last weight loss onset at 379 °C is attributed to the thermal decomposition of covalent bonds (C-OH, Si-O-Si and Si-O-C) and the cleavage of polymer backbones.

Figure 7: Thermogravimetric graphs of QDAPPO and QDA-IL membranes; a) percentage weight loss vs. temperature b) derivative weight (mg) vs. temperature

3.7 Mechanical properties

Mechanical stability is usually one of the critical challenges when the AEMs with high IEC are desired. In most cases, the high IEC leads to excessive membrane swelling and compromises the mechanical stability of AEMs due to weak interaction among the polymer chains. The mechanical properties of DA-IL membranes in both wet (membrane kept in water prior to testing) and dry states are shown in Figure 8a and b. It is apparent in general trend that the incorporation of IL into QDAPPO enhanced the mechanical properties. In dry states, upon incorporating IL into QDAPPO, the tensile strength (TS) and elongation at break (EB) firstly decrease and then increases (Figure 8a). As shown in Figure 8a, the dry QDA-IL membranes displayed TS and EB of 11-28.6 MPa and 3.3-12.6 % while the QDAPPO has the TS and EB of 14.9 MPa and 4.92 %, respectively. The addition of IL within QDAPPO matrix firstly weakens the strength and elongation at 10 % wt of IL and then further addition of IL enhances remarkably the EB, especially in wet conditions. The best explanation is that the introduction of IL at first decreases the hydroxyl groups which can maintain the membrane flexibility in dry condition owing to hydrogen bonds. In wet conditions, the EB increases with addition of IL up to QDA-IL2 membrane and then decreases from QDA-IL 3 to QDA-IL6 as a result of increasing pores density by IL in QDA-IL membranes. As the IL contents increases, the QDA-IL1 and QDA-IL2 gained the flexibility as a result of moderate crosslinking. Further addition of IL increases the pores density (free volume) in membrane matrix and consequently decreases the flexibility. In other words, the high density of pores in membrane matrix weakens the elongation at break. Compared the EB of membranes in both dry and wet condition (Figure 8b), there is a remarkable increase between the couple of QDA-IL membranes than in QDAPPO. This implies that WU has great impact on QDA-IL membranes. For example, the elongation at break of QDA-IL1 increased about 9 folds from 3.2% to 28.3% while QDA-IL2 increases from 6.11% to 46.47%, respectively.. In comparison to QDAPPO, the QDA-IL membranes are more flexible and tough in wet conditions which make them more suitable for various AEM applications.

Figure 8: Mechanical properties of QDAPPO and QDA-IL membranes in both dry and wet states; a) Tensile strength (TS), b) Elongation at break (EB)

4. Conclusion

Highly charge hierarchical porous anion exchange membranes were successful prepared by crosslinking quaternized poly (2-dimethylaminoethanol-N-2,3-dimethylphenyl oxide) and 3-methyl-1-(3-(triethoxysilyl)propyl)-1H-imidazolium chloride (Ionic liquid, IL). The obtained membranes are thin, mechanically stable and possess high ion exchange capacity for versatile anion exchange membranes based applications. In diffusion dialysis for acid recovery, the hierarchical porous membranes exhibited high performance, excellent membrane selectivity and superior acid recovery than the commercial DF-120 membranes and many others reported anion exchange membranes. We found that the proton diffusion coefficient increases with temperature up to 0.045 m h^{-1} at 65°C . These membranes are mechanically and thermally stable. This work presents a feasible strategy to construct gradient porous system, highly stable and high performance anion exchange membranes with controllable morphology. Therefore, by improving membrane composition and adjust pores size, ongoing study aim to expand application in salinity gradient energy harvesting techniques, desalination and fuel cells.

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