



Covalently cross-linked pyridinium based AEMs with aromatic pendant groups for acid recovery via diffusion dialysis



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ABSTRACT

In this study, the pyridinium anion exchange precursor was prepared by alkylation of 4-bromomethyl benzoic acid to pyridine and then the corresponding covalently cross-linked pyridinium based AEMs were obtained by esterification reaction through the prepared pyridinium salt and polyvinyl alcohol (PVA) as a base material in presence of tetraethoxysilane (TEOS) as a crosslinker. The prepared anion exchange membranes are characterized by FTIR, SEM, TGA and DMA. T_d values are in the range of 322–335 °C. The tensile strength (TS) ranges from 43.74 to 47.23 MPa and elongation at break (E_b) in the range of 262.59–474.44%. The acid dialysis coefficients (U_H) are in the range of $1.28\text{--}1.88 \times 10^{-2}$ m/h, greater than the well known commercial membrane DF-120 (9×10^{-3} m/h). The membrane containing 40 wt% of PVA has the highest separation factor (S) of 71.35. Note that the DD tests have been evaluated according to the membrane structure and its composition.

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1. Introduction

Globally, tremendous efforts are devoted to defeat serious issues related to wastes treatment. For example, waste waters generated from different discharged sources cause not only the environment pollution but reduce clean water availability and efficiency [1–4]. Considering various technologies which deal with waste water treatment, the membrane technology is of great significance [5,6]. Among others, the diffusion dialysis is a promising separation technique for acid or alkali recovery as it possesses the advantages of low energy consumption, easy operation and environmental benignity. However, there are still some disadvantages such as low treatment capacity and high water osmosis [7–10]. Notably, various membranes which are commercially available don't fulfill the desired properties to be used successfully in the diffusion dialysis. Some of them are hydrophobic with lower water retention capabilities while others are hydrophilic with higher swelling behavior [7,11]. Therefore, there is need to develop the well defined functional groups which maintain the membrane structure with desired properties [9,12].

One of the approaches to improve the membrane performance is to design the membrane structure consisted of both hydrophilic and hydrophobic behavior to enable the balance between the

dimensional stability and ions transport [13–16]. The attachment of aromatic pendant groups which contain the carboxylic groups could maintain the hydrophilicity of the membrane and guarantee the chemical and mechanical stabilities [17,18]. Also, the incorporation of cross-linking agents could help in reducing the membrane swelling [9,19,20].

It has been found that the quaternary ammonium functionality in heterocyclic ring or benzyl position presents relative instabilities so that their corresponding membranes show defects on their chemical stabilities [21]. Alternatively, the introduction of an alkyl spacer between the benzene ring and quaternary nitrogen in anion exchangers affects an increase in the chemical and thermal stability of the functional group. Compared to quaternary ammonium groups, the aromatic amines have good chemical and thermal stabilities. Similarly, (heterocyclic) aromatic amines are more stable than (heterocyclic) aliphatic amines. Herein, there are two factors which explain the choice of the heterocyclic aromatic amines: (a) the resonance stabilization of the free base form of aromatic amines. This resonance stabilization is a result of interaction of the unshared pair on nitrogen with the π (π) system of the aromatic ring. (b) The second factor is the electron withdrawing effect of the sp^2 hybridized carbons of the aromatic ring compared with the sp^3 hybridized carbons of aliphatic amines. This makes the unshared pair of electrons on nitrogen in an aromatic amine to be pulled toward the ring and, therefore, becomes available for protonation [22,23].

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Nomenclature

Abbreviations and acronyms

AEM	anion exchange membrane
ATR	attenuated total reflectance
DD	diffusion dialysis
DMA	Dynamic Mechanical Analysis
E_b	elongation at break
FT-IR	Fourier Transform Infra-red
IDT	initial decomposition temperature
IEC	ion exchange capacity
LER	linear expansion ratio

NMR	nuclear magnetic resonance
PVA	poly vinyl alcohol
S	separation factor
SEM	scanning electron microscopy
TEOS	Tetra Ethyl Ortho Silane
TGA	thermo gravimetric analysis
TS	tensile strength
U_{Fe}	dialysis coefficient of $FeCl_2$
U_H	dialysis coefficient of HCl
WU	water uptake

In our previous published work, the anion exchange membranes were fabricated based on alkoxy silane and 1-methyl imidazole; therefore the homogeneous, dense and compact membranes were obtained [7]. In the second work, the long chain hydrocarbons linked to pyridine were utilized to obtain homogeneous and flexible anion exchange membranes [24]. In this current work, the alkylation of heterocyclic aromatic groups on pyridine is adopted and the homogenous membranes with good chemical and dimensional stabilities are facilely obtained. The novelty of this work lies on the availability of aromatic pendant groups which play an important role in the restriction of ions with big size and therefore increase the separation factor of the membranes. During the material synthesis, the bromomethyl group of 4-bromomethyl benzoic acid is reacted in a nucleophilic substitution with pyridine and the pyridinium salt with aromatic pendant groups is synthesized. The anion exchange membranes were therefore prepared by the esterification reaction between acid groups of the synthesized material and hydroxyl groups of PVA (which is also as polymer backbone). In addition, the cross-linking of polymer chains is the most common way to improve mechanical stability of the membranes. Herein, the incorporation of TEOS enhances the mechanical and thermal stabilities of the membranes by controlling the membrane swelling nature [9,25,26].

Moreover, we have demonstrated that the behavior of the fabricated membranes was explained by an interesting relationship between physicochemical properties and composition for these membranes. On one hand, with silica content imbibed into the membrane, the mechanical properties are enhanced while by loading the pyridinium salt, the mechanical properties become poor but definitely balanced due to aromatic pendant groups [25,27]. On the other hand, silica and pyridinium salt content are favorable to obtain higher acid dialysis performances. The presence of $-COO^-$ groups could provide the channeling sites of ions passage through hydrogen bonding [14,20]. Also, the introduction of aromatic groups in the membranes could exhibit inferior ions transport especially the ones with relatively larger size and then will result in the increase of the separation factor of the membrane during diffusion dialysis [27].

After the membrane design and characterization, a simulated waste solution was used to test the membrane performance for acid recovery via diffusion dialysis as previously reported [7]. The results were then discussed according to the literature and compared to well known commercial membranes which are already on the markets [26,28].

2. Experimental section

2.1. Materials and reagents

Polyvinyl alcohol (PVA, 99%) was supplied by Shanghai Yuanli Chemical Co (Shanghai, China). The average degree of polymeriza-

tion was 1750 ± 50 (corresponding to a molecular weight of $77,000 \pm 2200$). Other chemicals were purchased from Shanghai-Sinopharm Chemical Reagent Co. Ltd. (China) and used without further purification. Note that all solvents were also used as received.

2.2. Anion exchange precursor synthesis

The anion exchange precursor was prepared by the following procedure: 4-bromomethyl benzoic acid was mixed with pyridine in bottom flask under vigorous magnetic stirring for a period of 12 h at room temperature [29,30]. The obtained product was precipitated in acetone and then filtered. The same product was dried in vacuum oven at $50^\circ C$ for a period of 24 h and subjected to NMR before keeping it in container for further use.

2.3. Membrane preparation and characterization

1 g of PVA was introduced in 19 g of dimethyl sulfoxide (DMSO) and heated in oil bath at $90^\circ C$ for a period of 4 h under vigorous magnetic stirring. The homogeneous and transparent PVA solution (5% weight) was obtained. The temperature was cooled down to $65^\circ C$ before addition of the synthesized anion exchange precursor with different mass quantities (10%, 20%, 30% and 40% relatively to PVA). The mixture of PVA solution and anion exchange precursor was stirred for about 1 h prior to addition of a small aliquot of HCl (1 M) to complete the esterification process. After a period of 16 h, the solution was titrated in order to confirm the esterification reaction between $-COOH$ of Pyridinium salt and $-OH$ of PVA. 10 g of solution was titrated by 0.1 M NaOH using phenolphthalein as indicator and the esterification degree was calculated by taking the ratio of reacted and initial product. Thereafter, 0.2 g of TEOS was added to the reaction mixture and the reaction took additional 8 h for homogeneous mixing and reaction completion. The final reactant solutions were then casted onto glass plate and dried at $60^\circ C$ for 24 h. The obtained membranes were then subjected to heat treatment by changing the temperature from $70^\circ C$ to $130^\circ C$ by raising $10^\circ C$ for 1 h as reported previously [7]. The membranes were labeled with Py-PVA 1, Py-PVA 2, Py-PVA 3 and Py-PVA 4 according to anion exchange contents (10%, 20%, 30% and 40%) respectively for further characterizations.

1H NMR spectra of anion exchange precursor and membrane solution were recorded on a Bruker DMX-300 NMR instrument at 300 Hz and DMSO was used as solvent. Fourier transform infrared spectroscopy (FTIR-ATR) of the membrane samples was recorded using FT-IR spectrometer (Vector 22, Bruker) with a resolution of 2 cm^{-1} and a spectral range of $4000\text{--}750\text{ cm}^{-1}$.

Thermal properties of the prepared membranes have been analyzed by using Thermo gravimetric analysis (TGA). TGA was conducted on a Shimadzu TGA-50H analyzer under air flow from $25^\circ C$ to $800^\circ C$ with a heating rate of $10^\circ C/\text{min}$. The mechanical

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