



# Enhancing acid recovery efficiency by implementing oligomer ionic bridge in the membrane matrix



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## ARTICLE INFO

### Article history:

Received 27 April 2016

Received in revised form

3 July 2016

Accepted 4 July 2016

Available online 7 July 2016

### Keywords:

Ionic channels

Anion exchange membrane

Multi-amine oligomer

Diffusion dialysis

## ABSTRACT

We report a strategy in improving the diffusion dialysis efficiency of anion exchange membranes (AEMs) by implementing a multi-amine oligomer bridge in the membrane matrix. The multi-amine oligomer, poly-dimethyl aminoethyl methacrylate (PD) was prepared via free radical polymerization, followed by partial quaternization with methyl iodide. The remaining tertiary amine groups were designed to react with benzyl bromide groups in the polymer brominated poly(2,6-dimethyl-1,4-phenylene oxide (BPPO) matrix, thus creating an intermolecular connection. The intermolecular connection serves as crosslinks and also helps to regulate the interconnectivity of the hydrophilic regions. By tuning the molecular weight and the remaining tertiary amine groups within PD, series of AEMs were fabricated. These membranes show potential in recovering waste acid via diffusion dialysis. For example, membrane M-5 shows an extraordinarily high separation factor ( $S_{H/Fe}$ ) of  $\sim 2074$  along with acceptable proton dialysis coefficient ( $U_H = 0.0098$  m/h). The  $S_{H/Fe}$  is much higher than that of the conventional quaternized poly(2,6-dimethyl-1,4-phenylene oxide) (QPPO) membrane without oligomer cross-linker ( $U_H = 0.0080$ – $0.0132$  m/h,  $S_{H/Fe} = 5$ – $60$ ). The improvement in diffusion dialysis efficiency could be attributed to the improved interconnectivity of the hydrophilic regions, which stems from the incorporation of inter-chain ionic bridge.

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## 1. Introduction

Sulfuric acids ( $H_2SO_4$ ) are widely used in metallurgical and chemical processes and large quantities of waste solutions containing free  $H_2SO_4$  and metallic ions are therefore produced [1]. For example, to manufacture 1 t of titanium white, 200–400 t of waste solution composed of  $H_2SO_4$  (10–20%),  $FeSO_4$  (15–20%) will be produced [2]. Disposal of this solution not only leads to environmental pollution, but also results in loss of valuable chemicals. Diffusion dialysis (DD), which is driven by the concentration gradient between two sides of the membrane, provides an attractive method for acid recovery from the viewpoint of energy saving and environment protection [3–5].

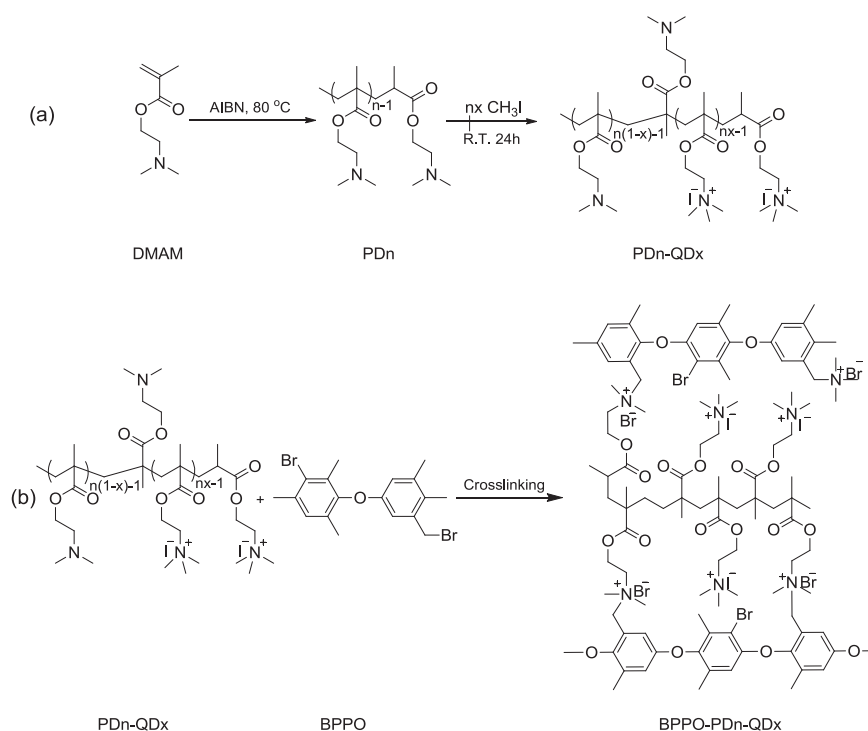
In a typical acid recovering process via DD ( $H_2SO_4/FeSO_4$  mixture), anions in the waste solution, i.e.  $SO_4^{2-}$ , are allowed to transport across the membrane driven by concentration gradient due to the attraction of positive fixed groups in anion exchange membranes (AEMs). Nevertheless, the cations, such as  $H^+$  and  $Fe^{2+}$  are rejected to some extent because of electric repulsion. To

equilibrate the charge difference across the membrane,  $H^+$  ions are preferentially dragged to the water side because of their smaller size, lower valence state and higher mobility than  $Fe^{2+}$  [6–8]. Consequently, acids ( $H_2SO_4$ ) would be enriched in the water side, while salts ( $FeSO_4$ ) are more likely to retain in the waste solution. The recovery of acid ( $H_2SO_4$ ) from waste solution is therefore fulfilled.

According to the above-mentioned analysis of DD process, the AEM plays a critical role in determining the separation efficiency [9–11]. Practically, the separation efficiency is characterized by the dialysis coefficient ( $U$ ) and separation factor ( $S_{H/Fe}$ ).  $U$  represents the mass transfer dialysis coefficient and it can be understood as the average moving velocity of ions within membrane matrix. So in this manuscript,  $U_H$  represents the average moving velocity of  $H^+$  and  $U_{Fe}$  represents the average moving velocity of  $Fe^{2+}$ . While  $S_{H/Fe}$  is defined as the ratio of proton dialysis coefficient ( $U_H$ ) to ferrous dialysis coefficient ( $U_{Fe}$ ). It reflects the selectivity for  $H^+$  and  $Fe^{2+}$  of the testing membrane. An ideal diffusion dialysis membrane should therefore possess high  $U_H$ , high  $S_{H/Fe}$  and high mechanical strength [7,8,12,13]. To recover  $H_2SO_4$  from the waste solution, an AEM composed of the fixed groups (i.e. quaternary ammonium (QA) groups here) and inert polymer backbone is needed. When the AEM is in contact with water, the fixed groups

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**Scheme 1.** Preparation of BPPQ-PDn-QDx.

would absorb water due to its hydrophilicity. The AEM can then be divided into three regions, the charged region (water surrounded QA groups), swelled region and hydrophobic polymer region. [14] The charged and swelled regions contribute to the transfer and separation of anions and cations, while the hydrophobic polymer region maintains the membrane integrity [4, 7, 15–21].

In separating  $H^+/Fe^{2+}$ , electric repulsion is anticipated when the cations (either  $H^+$  or  $Fe^{2+}$ ) are in contact with QA groups. Due to higher valence state than  $H^+$ ,  $Fe^{2+}$  will be subject to greater resistance, thus making it more difficult for  $Fe^{2+}$  to penetrate [6]. For this point of view, one QA group serves as one exclusion site, fulfilling a one-time separation. Therefore, to obtain high  $S_{H/Fe}$  value, a great amount of QA groups, i.e. high ion exchange capacity (IEC) value is expected. However, when the IEC value of an AEM increases, the swelling of the membrane is increased, leading to the increase of swelled regions. Although it leads to higher ion transfer rate (higher  $U_H$ ), the swelled region mainly composed of absorbed water shows no separation for  $H^+/Fe^{2+}$ , thus leading to the decrease in  $S_{H/Fe}$ . Moreover, excessive membrane swelling will bring about the decrease in membrane mechanical strength.

A more reasonable way in improving the DD efficiency of an AEM for acid recovery is to orderly arrange the QA groups to the largest extent and to restrict the membrane swelling at the same time. In this contribution, we found a way to crosslink the AEM and in the meantime to arrange the QA groups in a more linear order. Provided the QA groups are arranged in a more linear way, they will aggregate to form the ionic channel and serves as “ionic exclusion column” to realize a continuous  $H^+/Fe^{2+}$  separation. A higher  $S_{H/Fe}$  is therefore obtained. The interconnected ionic channel also brings about the interconnectivity of the swelled region and they both result in the increase of  $H^+$  transfer rate i.e.  $U_H$ . Additionally, the membrane swelling would be restrained by crosslinking.

We firstly synthesized an oligomer crosslinking agent, polydimethyl aminoethyl methacrylate (PD) via free radical polymerization. It was then incorporated in the membrane matrix to construct an inter-chain crosslinking and also served to form a

linear ionic array for the separation of  $H^+$  and  $Fe^{2+}$ . Tough and ductile, light yellow to brown colored membranes with a thickness of around 30  $\mu m$  were obtained by solution casting. Properties of all membranes such as water uptake (WU), linear swelling ratio (LSR), mechanical strength, thermal properties, and morphology are investigated. Moreover, DD experiments for  $FeSO_4/H_2SO_4$  aqueous mixture show extraordinarily high  $S_{H/Fe}$  of  $\sim 2074$  relative to the commercial DF-120 membrane ( $U_H=0.009$  m/h,  $S_{H/Fe}=18.5$  at 25 °C) [16].

## 2. Experimental

### 2.1. Materials

Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPQ) with a degree of benzyl bromination substitution of 0.52 was supplied by Tianwei Membrane Corporation Ltd. (Shandong, PR China) and was purified before use. The detailed purification procedure and characterization were shown in the supporting information (SI, Fig. S1). N-methyl pyrrolidone (NMP), diethyl ether (DEE), sodium chloride (NaCl), tetrahydrofuran (THF), sodium hydroxide (NaOH), sodium sulfate ( $Na_2SO_4$ ), anisole, and acetonitrile are of analytical purity and purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, PR China). All these reagents were used as received. Trimethylamine (TMA), methyl iodide ( $CH_3I$ ), n-hexane were purchased from Energy Chemical Shanghai, PR China) and used as received. Reagent grade dimethyl aminoethyl methacrylate (DMAM, J & K Chemical Technology Ltd.) was purified by alumina column chromatography and stored in refrigerator for further use [22]. 2, 2-azobisisobutyronitrile (AIBN) (Sinopharm Chemical Reagent Co. Ltd) was recrystallized from methanol, dried under vacuum at room temperature (R. T.) and stored at  $-4$  °C [23].

### 2.2. Radical polymerization of DMAM

Polymerization of DMAM was carried out in de-oxygenated

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