

# Stable cycloaliphatic quaternary ammonium-tethered anion exchange membranes for electrodialysis

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## ARTICLE INFO

### Keywords:

Anion exchange membranes  
Brominated PPO  
N-methylpiperidine  
Alkaline stability  
Electrodialysis

## ABSTRACT

In this work, we have investigated a series of anion exchange membranes (AEMs) based on brominated poly(2,6-dimethyl-1,6-phenylene oxide) (BPPO) tethered with three saturated heterocyclic quaternary ammonium groups (QAs) of 1-methylpyrrolidine (MPY), N-methylpiperidine (MPRD), and 4-methylmorpholine (MMPH) for electrodialysis (ED) applications, respectively, along with BPPO with trimethylamine (TMA) and Neosepta AMX made for comparison. Our investigations demonstrate that the optimized BPPO-MPRD, having an ion exchange capacity of 1.67 mmol g<sup>-1</sup>, is highly stable in aqueous KOH (1 mol L<sup>-1</sup>) with ion exchange capacity retention ratio of 85.1% and hydroxide conductivity retention ratio of 80.3% at 60 °C for over 15 days, relative to other heterocyclic amine decorated AEMs. In ED application process, BPPO-MPRD shows the NaCl removal ratio of 98.8% and energy consumption of 12.58 kWh kg<sup>-1</sup>, outperforming the Neosepta AMX (97.4% & 15.76 kWh kg<sup>-1</sup>). The results demonstrate that the as-prepared BPPO-MPRD AEM can be applied in ED.

## 1. Introduction

Among many available separation techniques, both reverse osmosis (RO) and electrodialysis (ED) have been considered as the commonly-used desalination processes in the field of water treatment [1, 2]. Relative to RO filtration with high pressure requirements, ED process depending on the ions transport through selective separators, can operate in an electrical field at the reduced energy consumption [3]. Owing to the various advantages of low cost fabrication, eco-friendly design, easy as well as low-energy consuming operation etc., the development of ED has already shown the vast application prospect for making safe drinking/process water from the brackish and seawater, separation of the hazardous chemicals from waste water streams, and recovery of the useful materials from salt production and effluents etc. [4–6]. Also, ED has been widely applied in food, chemical and pharmaceutical industries, to demineralize valuable solutions for fluid purification [7, 8].

Anion exchange membranes (AEMs) have been widely investigated to accomplish the selective permeation of anions in the fields of ED, diffusion dialysis (DD), redox flow battery (RFB), fuel cell (FC), electro-membrane reactor and chlor-alkali process [9, 10] etc. In particular,

AEMs, as the key component of ED, allow the effective anion transportation via an electrostatic interaction but significantly suppressing the passing of cations [1–3]. Thus, high-performance AEMs with high-conductivity, desired selectivity, good (chemical, thermal, oxidative) stability are urgently required for the practical applications above-mentioned [1]. So far, numerous types of polymers have been employed for AEM fabrication, for example, polystyrene [11, 12], polyether imide [13] polysulfone [14], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [15], poly(arylene ether) [16], poly(phthalazinone ether ketone) (PPEK) [17], and poly(phthalazinone ether sulfone ketone) (PPESK) [18] etc. However, most of the efficient AEMs are fabricated via highly carcinogenic and hazardous chloromethylation (CME) of aromatic rings attached to polymer chains, followed by quarter of amination reaction [8]. In addition, the preparation process is usually time-consuming and sophisticated. Therefore, it is highly desirable to prepare cost-effective AEMs through safer routes without using the hazardous materials.

Apart from the concerns, the insufficient stability of most AEMs also limits their practical applications under severe condition (e.g., strong alkaline conditions). The long-term alkaline stability is crucial for long-life AEMs [19, 20]. Thus, stable AEMs are highly desirable. It is long-known that trimethylamine (TMA) group-based AEMs have been widely

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applied, however, the alkaline stability of this positively charged TMA groups greatly hinders the further applications in strong alkaline conditions, due to the degradations resulted from polymer backbone chain scission, Hoffmann elimination and  $S_N2$  substitution of cationic side chains [21]. So far, many AEMs with QAs of imidazolium, guanidinium and phosphonium groups have been developed for alkaline fuel cell (AFC) [22–24]. The results illustrate that the alkaline resistance properties can be enhanced, however, it is still limited. For example, it is reported that, in 1–3 M KOH/NaOH aqueous basic solutions at 60 °C, imidazolium-AEMs are not as stable as expected [25]. Recently, Dang et al. [26] have revealed that AEMs with the cycloaliphatic QAs like *N*-methylpiperidine (MPRD) on pentyl spacer of AEMs show the desirable alkaline stability in 1 M NaOH at 90 °C within 16 d. This excellent alkaline stability can be due to the  $\beta$ -protons with the C–C bond of the six-membered ring of MPRD rotationally restricted by the its geometry on the elimination transition state.

The accessible advantages of cycloaliphatic QAs have inspired us to investigate the potential application in ED. Also, considering accessible stable BPPO having abundant  $-\text{CH}_2\text{Br}$  functional groups, a series of AEMs has been fabricated herein, by using BPPO tethered with three different saturated-heterocyclic QAs (-MPY, -MPRD and -MMPH) for ED application. Though the alkaline stability of MPY, MPRD and MMPH has been recently revealed by Dang et al. [26], the relationship between structure, properties and ED performance of as-prepared AEMs has not been investigated yet. Herein, the physico-chemical properties (e.g., ion exchange capacity, water uptake, linear expansion ratio, thermal stability, mechanical stability, alkaline stability, area resistance and transport number) of as-prepared AEMs have been systematically investigated for ED process, along with the commercial Neosepta AMX made for comparison.

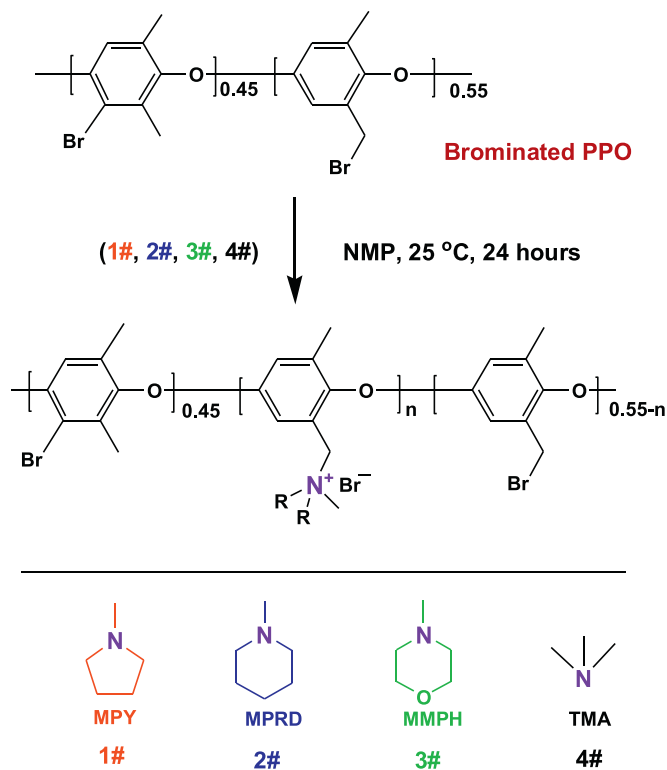
## 2. Experimental

### 2.1. Materials

All chemicals, including trimethylamine (TMA), 1-methylpyrrolidine (MPY, 97%), 1-methyl-2-pyrrolidone (NMP, 99.5%), *N*-methylpiperidine (MPRD, 99%), 4-methylmorpholine (MMPH, 99.5%), sodium chloride (NaCl) and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were purchased from Aladdin Reagent Co. Ltd., Shanghai, China, and used without further purification. Brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) having aryl substitution degree of 0.42 and benzyl substitution degree of 0.55 was provided by Tianwei Membrane Co. Ltd., Shandong of China. Deionized (DI) water was used throughout the experiments. Commercial AEM Neosepta AMX and CEM Neosepta CMX were purchased from FUJIFILM Corp. Japan.

### 2.2. Membranes preparation

BPPO-based AEMs having trimethylamine (TMA) and tethered with different heterocyclic QA groups were fabricated by using solution casting method [27]. The as-obtained AEMs (designated BPPO-X, where X represents the different amines used for quaternisation, see Scheme 1) were denoted as BPPO-MPY, BPPO-MPRD, BPPO-MMPH, BPPO-TMA, respectively. Herein, we take the fabrication of BPPO-MPRD AEM as an example. 2.0 g BPPO was dissolved in 10 mL NMP solvent to form a homogeneous solution, followed by adding *N*-methylpiperidine (MPRD) to the BPPO/NMP solution in a mole ratio of 1:1 and stirring for 24 h at room temperature. The resultant solution was casted onto a clean glass plate and thermally treated at 60 °C for 8 h, rendering a polymer film peeled off from the glass. Subsequently, the as-prepared AEM was thoroughly washed with deionized water and further dried at 80 °C for 24 h.



**Scheme 1.** Preparation of BPPO-based AEMs with different QA groups (BPPO-MPY, BPPO-MPRD, BPPO-MMPH, BPPO-TMA).

### 2.3. Membrane characterization

#### 2.3.1. $^1\text{H}$ NMR and FTIR spectra

$^1\text{H}$  NMR spectra were recorded on a NMR spectrometer (Bruker AVANCE III 500 MHz) at room temperature, using dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) and chloroform D ( $\text{CDCl}_3$ ) as solvents, respectively. FTIR spectra of dried AEMs were recorded by employing Nicolet 6700 spectrometer. The structure was further analyzed by using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD), respectively. The membrane samples were dried under vacuum for 24 h (80 °C) before characterization.

#### 2.3.2. Thermal stability

The thermal stability of as-prepared AEMs was undertaken on Netzsch (STA 449C, Germany) thermal analyzer under  $\text{N}_2$  flow with a heating rate of  $10\text{ °C min}^{-1}$  from 30 to 700 °C.

#### 2.3.3. Ion exchange capacity (IEC)

The three pieces of dry membrane samples was accurately weighed after being dried at 60 °C under a vacuum for 24 h, respectively. Then the samples were converted to the  $\text{Cl}^-$  form by soaking them in 0.10 M NaCl for two days. Subsequently, samples were rinsed carefully with DI water, to remove the excess NaCl, followed by immersing in 0.05 M  $\text{Na}_2\text{SO}_4$  for 24 h. The amount of chloride ions liberated was measured by titration with 0.1 M  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$  as indicator. The IEC values were calculated using Eq. (1):

$$\text{IEC} = \frac{C_{\text{AgNO}_3} \times V_{\text{AgNO}_3}}{W_{\text{dry}}} \quad (1)$$

where  $C_{\text{AgNO}_3}$  represents the concentration of the  $\text{AgNO}_3$  solution (M),  $V_{\text{AgNO}_3}$  represents the volume of the  $\text{AgNO}_3$  solution (mL), and  $W_{\text{dry}}$  represents the mass of the dried sample (g).

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