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# A mechanically robust anion exchange membrane with high hydroxide conductivity



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## ABSTRACT

As a key component of various electrochemical systems, such as alkaline polyelectrolyte fuel cells (APEFCs), flow batteries and electrolyzers, anion exchange membranes (AEMs) need to be both mechanically robust and highly conductive to hydroxide ions. In this work, a polyelectrolyte with a particular polymer structure was designed by combining phase-separation architecture and a crosslinking strategy to improve both the mechanical properties and hydroxide conductivity. The side chain of this type of polyelectrolyte was incorporated by two quaternary ammonium groups and terminated with a cross-linkable unsaturated bond. After being simply heated at 80 °C for 24 h, the crosslinked AEMs exhibited enhanced tensile strength ranging from 23.1 MPa to 14.7 MPa under hydrated conditions. These values are several times higher than the values of conventional AEMs. As a result of the high flexibility and hydrophilicity of the dual-cation-functionalized side chain, an outstanding hydroxide conductivity was observed (43 mS/cm at room temperature and 88.7 mS/cm at 80 °C). Also considering its good dimensional stability and satisfying alkaline tolerance, this strategy combining phase separation architecture and crosslinking has perfectly solved the several obstacles blocking the development of AEMs and thus possesses a great potential for practical application.

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## 1. Introduction

Anion exchange membranes are key components of various electrochemical systems for energy conversion and energy storage, such as alkaline polyelectrolyte fuel cells (APEFC) [1], flow batteries [2], and electrolyzers [3]. However, the further development of AEMs is still blocked by their low anionic conductivity in relation to proton-exchange membranes (Nafion<sup>®</sup> for example). An ideal anion exchange membrane should possess the advantages of excellent mechanical properties, good dimensional stability, high hydroxide conductivity and adequate hydroxide stability. However, despite the numerous efforts devoted to the fabrication of high-performance AEMs, it is very difficult to simultaneously obtain these four key properties. It is well documented that there is a direct relation between hydroxide conductivity and ion-exchange capacity (IEC); thus, enough ion-conducting groups (typically quaternary ammonium groups for an AEM) need to be attached onto the main chain of the polymer when pursuing high hydroxide conductivity. However, a high IEC value usually leads to the

undesired decline of the dimensional stability and mechanical properties. Thus in this study, we focus on detangling this dilemma and prepare AEMs with high hydroxide conductivity as well as good mechanical properties.

A crosslinking strategy is usually applied in the design of polymer architecture to obtain mechanically robust AEMs with improved dimensional stability [4]. A polymer precursor bearing cross-linkable moieties, such as an unsaturated bond [5,6] or benzyl halide [7], was first synthesized, and the crosslinking reaction was usually initiated during the membrane-forming process to avoid gelation. However, despite the restricted swelling ratio and enhanced mechanical properties, the previously reported crosslinked AEMs often exhibit poor hydroxide conductivity because of the lack of well-defined ion-conducting channels and reduced water uptake. It is well documented that water molecules play a crucial part in the conduction of hydroxide ions, but enhancing the water content of the crosslinked AEM is obviously unfeasible to disentangle the conductivity and mechanical properties problem. Therefore, facilitating the formation of well-defined ion-conducting channels of AEMs now seems to be the best way to obtain AEMs with both good mechanical properties and high hydroxide conductivity.

As we know, the hydrophilicity and hydrophobicity discrimination of different polymer segments can lead to self-assembled

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nanophase separation of AEMs, resulting in ion-conducting channels containing a high density of ion-conducting groups. As demonstrated by atomic force microscopy (AFM) [8], transmission electron microscopy (TEM) [9] or small-angle X-ray scattering [10], well defined nanophase separation is usually directly correlative to a high hydroxide conductivity of AEM. To date, numerous strategies have been developed to enhance the nanophase separation ability of anion-exchange membranes, which can be separated into two categories, enhancing the flexibility of functional side chains [11,12] and improving the hydrophilicity of the ionic segment [13,14]. However, these two strategies could be combined by densely incorporating quaternary ammonium groups into the flexible side chains of AEMs [15]. Due to the high flexibility of aliphatic side chains and the enhanced hydrophilicity resulting from a high density of ion-conducting groups, this as-designed polyelectrolyte is predicted to exhibit an excellent ability to self-assemble and to possess well-defined ion-conducting channels.

Further, to synthesize AEMs with good mechanical properties, excellent dimensional stability, high hydroxide conductivity and adequate alkaline stability, a synthesis that combines both a cross-linking strategy and phase-separation architecture needs to be demonstrated. Previously, crosslinked comb-shaped AEMs with good mechanical properties were prepared by Hickner and co-workers [5]. Side-chain-type crosslinked AEMs were also synthesized in our group [6]. However, only one quaternary ammonium group was incorporated into the side chain of these AEMs. In this study, we have designed a specific functional side chain containing two quaternary ammonium groups to enhance the hydrophilicity and flexibility of the ionic segment, thus facilitating the formation of well-defined nanophase segregation. Moreover, this highly flexible and hydrophilic side chain was terminated with one unsaturated bond that produces a high self-polymerization reactivity, thus the crosslinking reaction can occur during the membrane forming process. Afterwards, the as-designed AEMs were characterized by AFM to verify the formation of inter-connected ion-conducting channels. The hydroxide conductivity, mechanical properties, dimensional stability and alkaline tolerance of the membranes were also investigated. Due to the combination of a cross-linking strategy and phase-separation architecture, the resulting AEMs were demonstrated to be both mechanically robust and to have a high hydroxide conductivity, thus providing a new direction for synthesizing high-performance AEMs.

## 2. Experimental section

### 2.1. Bromination of poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO)

PPO was brominated as previously reported [10] via free-radical bromination. A typical synthetic procedure is described as follows: To a stirred solution of PPO (6 g, 50 mmol) in chlorobenzene (60 mL) was added N-bromosuccinimide (NBS) (3.6 g, 20 mmol) and 2,2-azobis(2-methylpropionitrile) (0.3 g). The reaction mixture was heated at 140 °C for 8 h. Afterwards, it was poured into excess ethanol to form a light-brown precipitate of BPPO. Then, the polymer was re-dissolved in chloroform (60 mL), followed by precipitation in ethanol. After being dried at 60 °C for 48 h, BPPO was obtained as light brown fibers. The NMR spectrum of BPPO is shown in Fig. S1, employing  $\text{CDCl}_3$  as the solvent. Signal 1 in the spectrum of BPPO is assigned to the protons of  $-\text{CH}_2-\text{Br}$ , suggesting the successful bromination of PPO. The degree of bromination of BPPO was calculated based on NMR spectrum according to the previously reported literature [10].

### 2.2. Synthesis of the tertiary-amine-terminated polymer precursor (TMAQAPPO)

First, 1 g of the bromination product of poly (2,6-dimethyl-1,4-

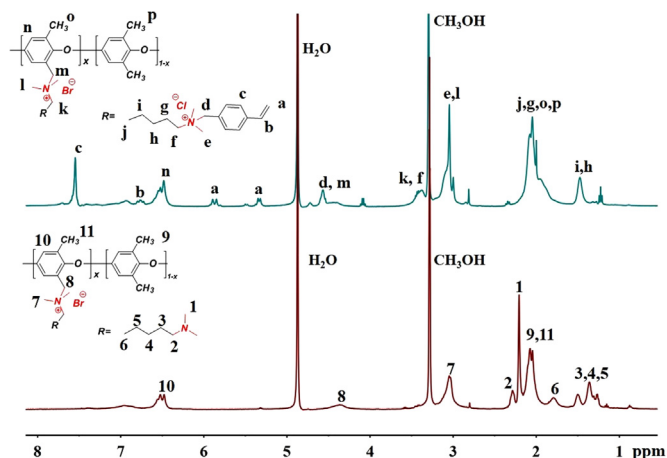


Fig. 1. NMR spectra of TMAQAPPO and VBBQAPPO polyelectrolytes (in  $\text{CD}_3\text{OD}$ ).

phenylene oxide) (BPPO) was dissolved in 15 mL of NMP. The resulting solution of BPPO was added to a stirred solution of N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA, 5 equiv) in NMP (15 mL). After being stirred at room temperature for 24 h, the TMAQAPPO was obtained by precipitating into ether followed by filtration. The resulting polymer was washed with ether three times and then dried under a vacuum for 24 h. The NMR spectrum of the TMAQAPPO employing  $\text{CD}_3\text{OD}$  as the solvent is shown in Fig. 1.

### 2.3. Synthesis of vinylbenzyl-terminated bi-cations containing polyelectrolytes (VBBQAPPO)

To a stirred solution of TMAQAPPO (1 g) in NMP (15 mL) was added 4-vinylbenzyl chloride (VBC, 3 mL). After being stirred at room temperature for 24 h, VBBQAPPO was obtained by precipitating into ether followed by filtration. The resulting VBBQAPPO was washed with ether for three times and then dried under a vacuum at room temperature for 24 h. The NMR spectrum of VBBQAPPO employing  $\text{CD}_3\text{OD}$  as the solvent is shown in Fig. 1.

### 2.4. Synthesis of quaternized poly(2,6-dimethyl-1,4-phenylene oxide) AEM (QPPO)

To a stirred solution of BPPO (1 g) in NMP (15 mL) was added an aqueous solution of trimethylamine (TMA, 1.5 equiv). After being stirred at room temperature for 24 h, a QPPO AEM was obtained by directly casting this resulting solution onto a glass plate followed by heating at 60 °C for 24 h. The NMR spectrum of QPPO was shown in Figure. S2 employing  $\text{DMSO}-d_6$  as the solvent. Signal 1 and signal 5 are assigned to the protons of  $\text{Ph}-\text{CH}_2-\text{N}^+$  and  $\text{N}^+-\text{CH}_3$ , respectively. Key properties of QPPO membrane are listed in Table S1 as well.

### 2.5. Fabrication of crosslinked AEMs

One gram of the above-mentioned VBBQAPPO was dissolved in 15 mL of NMP and then cast onto a clean glass plate followed by heating at 80 °C for 24 h. The resulting tough and transparent membrane was peeled off. The crosslinked AEMs thus obtained were called CBQAPPO-x (Crosslinked Bi-Quaternary Ammonium containing PPO-based AEMs). Four AEMs with different IEC values were prepared for which the variable x was numbered 1, 2, 3 and 4 according to the ranking of IEC values. For example, the membrane with the highest IEC value was named as CBQAPPO-4. The key properties of CBQAPPO-x membranes were listed in Table S1.

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