



# Dual-cation comb-shaped anion exchange membranes: Structure, morphology and properties



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## ABSTRACT

Anion exchange membranes (AEMs) are employed as the gas separator and hydroxide ion conductor between the anode and the cathode of alkaline polyelectrolyte fuel cell (APEFC). Highly conductive and stable AEMs are urgently needed in order to achieve satisfactory fuel cell performance. Nevertheless, the low hydroxide conductivity remains major challenge that limits the development and application of APEFC. In order to improve the hydroxide conductivity of AEMs, highly ordered ion conducting channels must be constructed within the membrane matrix. In this study, an AEM with particular polymer structure was designed to achieve fine ion conducting channels by facilitating the hydrophilic-hydrophobic phase separation. Concretely, the side chain of this polyelectrolyte contains two quaternary ammonium groups and terminates with one long hydrophobic tail. Ascribing to the enhanced nano-phase separation ability, inter-connected ion conducting channels were observed by AFM as well as SAXS. A high hydroxide conductivity of 47 mS/cm at 25 °C and 85 mS/cm at 80 °C was achieved. In addition, when applied in an APEFC system, the synthesized AEM showed an outstanding peak power density of 369.3 mW/cm<sup>2</sup>. Good alkaline tolerance, lowered water uptake and swelling ratio were also observed attributing to its carefully designed polymer structure.

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## 1. Introduction

Polyelectrolyte fuel cell (PEFC) is recognized as one promising energy generating technology for its distinct advantages like high conservation of energy, low operation temperature, fuel diversity and so on [1]. For the past decades, the research interests of fuel cell community were mainly focused on the development of the acidic polyelectrolyte fuel cell which depends on the precious metal catalyst (Pt) and the expensive perfluorinated sulfonic acid membrane. In order to lower the equipment cost and further broaden the application of fuel cell technology, significant advance has been made by employing an anion exchange membrane (AEM) instead of a cation exchange membrane between the cathode and the anode, namely alkaline polyelectrolyte fuel cell (APEFC) [2]. Because of the faster kinetics of oxygen reduction under alkaline environment, Pt is possible to be replaced by other non-precious catalyst like Ni and Co [3].

However, the development and application of APEFC were still

challenged by the insufficient hydroxide conductivity of the anion exchange membrane. This has evoked extensive research interests towards exploring the structure-property relationship of AEM in order to achieve high conductivity through polymer structure optimization [4]. It has been well documented that formation of well-connected anion conducting channels is the key factor that dominated the conductivity of AEM [5]. Because of the hydrophilic-hydrophobic discrimination between the water repellent polymer backbone and the hydrophilic cationic segments, the anion conducting groups of AEM tend to aggregate together, allowing phase separation in nano-scale. The ionic domains formed during the phase separation process contain high density of ion conducting groups, thus are considered to be the main pathway for anion conduction.

Over the last decade, numerous strategies [6–11] have been developed aiming to achieve good nano-phase separation and well-connected ion conducting channels. For example, Jannasch and co-workers [9] found that by densely grafting the quaternary ammonium groups (QA groups) onto one particular segment of polymer backbones, the nano-phase separation ability and the hydroxide conductivity could be enhanced because of the increased hydrophilic-hydrophobic discrimination [9,12–16]. Bai and

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co-workers also reported one highly conductive AEM with three QA groups locating on one pendent phenyl ring [17]. There is a very unusual phenomenon that high hydroxide conductivity was achieved while no nano-phase separation was observed by SAXS. The author considered that the decreased distance between QA groups, which can efficiently facilitate the hopping conduction of hydroxide ions, is the main reason for the observed high conductivity.

Another strategy to improve the nano-phase separation of AEM is to enhance the flexibility of the functional side chain. Previously in our lab [18], one side chain type AEM with a flexible aliphatic spacer between ion conducting group and polymer main chain have been prepared and proved to possess enhanced hydroxide conductivity. Recently, a series of side chain type AEMs have been reported [19–21], all demonstrating that the flexibility of side chain, which decides the mobility of ion conducting group, also has profound influence on the nano-phase separation ability and the anion conductivity of AEM.

As an upgrade for the side-chain type AEM, Zhuang's research group introduced two QA groups into one same side chain of anion exchange membrane [22]. Improved alkaline stability was observed due to the decreased grafting ratio of cationic group on the polymer backbone. Afterwards, our group reported AEM with the dual-cation [23] and tri-cation containing side chain [24]. Excellent nano-phase separation as well as high hydroxide conductivity were observed because of the increased polar difference between the hydrophilic side chain and the hydrophobic polymer backbone. Yan and co-workers further increased the number of cation on the side chain. Changing trend of the conductivity with the side chain functionalization degree was investigated [25]. Hickner's research group evaluated the properties of a series of AEMs with the multi-cation functionalized side chain, excellent fuel cell performance was observed for the tri-cation based AEM [26].

Hickner and co-workers [27] also prepared the comb-shaped AEM by reacting brominated poly (2,6-dimethyl-1,4-phenylene oxide) with one tertiary amine bearing long aliphatic chain. Excellent nano-phase separated morphology was observed by small angle X-ray scattering (SAXS) due to the unique polymer structure with the hydrophilic main chain and the hydrophobic side chain [10,28,29]. Zhuang and co-workers [6] reported another comb-shaped AEM prepared by attaching the aliphatic chain onto the polymer backbone but separately from QA group, outstanding high temperature hydroxide conductivity even comparable to the Nafion<sup>®</sup> was achieved.

Inspired by these works, we have designed one dual-cation

comb-shaped polyelectrolyte which is expected to possess the excellent nano-phase separation ability and the resultant high hydroxide conductivity. As depicted in Fig. 1b, a long aliphatic tail was introduced to the end of the side chain in order to ensure the good nano-phase segregation. The high mobility of QA group resulting from the flexibility of the side chain can also facilitate the aggregation of the ionic segments. Besides, two QA groups were inserted between the polymer main chain and the aliphatic tail in order to increase both the side chain hydrophilicity and the functional group density in the ion conducting channels.

Experimentally, two steps of Menshutkin reactions were employed to prepare this dual-cation comb-shaped polyelectrolyte. Afterwards, AEMs with this unique polymer structure were investigated by the atomic force microscopy (AFM) and the small angle X-ray scattering (SAXS) to detect their nano-phase separation. Hydroxide conductivities, fuel cell performance, water uptake, swelling ratio, mechanical properties as well as alkaline tolerance were also characterized.

## 2. Experimental section

### 2.1. Materials

Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) with an intrinsic viscosity of 0.57 dl/g in chloroform at 25 °C was manufactured by Asahi Kasei Chemicals Corporation (Japan) and kindly supplied by Tianwei Membrane Company (Shandong, P.R. China). PPO was brominated as previously reported [23,24] via free radical bromination. Bromination degree of brominated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) was calculated according to <sup>1</sup>H NMR Spectrum (Fig S1). N-bromosuccinimide (NBS), 2,2'-azobis (2-methylpropionitrile) (AIBN), N,N,N',N'-tetramethyl-1,6-hexanediamine (TMHDA), 1-bromooctadecane were purchased from Energy Chemical Co. Ltd. (Shanghai, P.R. China) and used as received. N-methyl-2-pyrrolidolone (NMP, AR), diethyl ether, chlorobenzene, ethanol, chloroform, toluene, acetonitrile, Hydrochloric acid (HCl) aqueous solution (37% AR), sodium chloride (AR), sodium hydroxide (AR) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>, AR) were purchased from Sinopham Chemical Reagent Co. Ltd. Deionized water was used throughout.

### 2.2. Synthesis of N-(6-(dimethylamino)hexyl)-N,N-dimethyloctadecan-1-aminium (DMAQA-C18)

DMAQA-C18 was prepared according to the previously reported

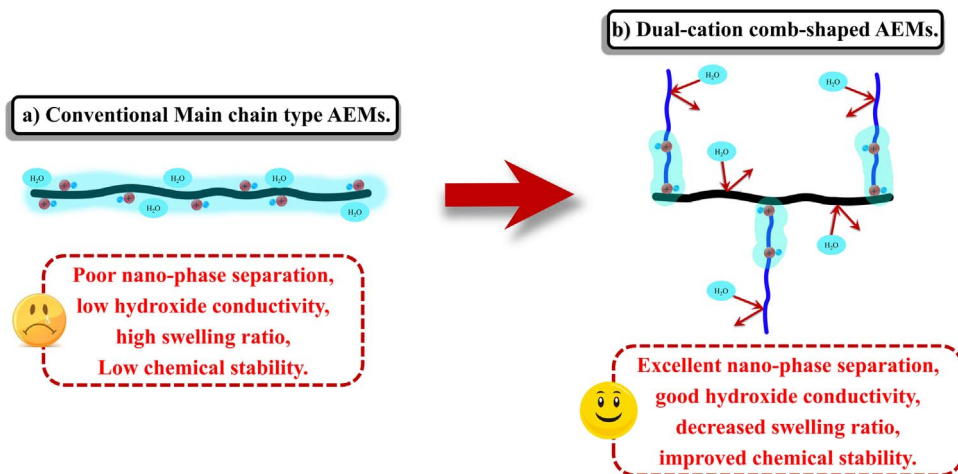


Fig. 1. Schematic illustration of (a): conventional main chain type AEMs. (b): dual-cation comb-shaped AEMs prepared in this work.

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