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## Full Length Article

# Comparison of alkaline stability of benzyltrimethylammonium, benzylmethylimidazolium and benzyldimethylimidazolium functionalized poly(arylene ether ketone) anion exchange membranes



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## ABSTRACT

The alkaline stability of benzyltrimethylammonium, benzylmethylimidazolium and benzyldimethylimidazolium functionalized poly(arylene ether ketone) anion exchange membranes (AEMs) were investigated by conductivity change and NMR experiments. The corresponding small molecular model compounds were synthesized and used to determine the degradation degree of benzyltrimethylammonium, benzylmethylimidazolium and benzyldimethylimidazolium cations. The results showed only 7% of benzyltrimethylammonium model compound degraded in 1 M NaOH at 60 °C; whereas, benzylmethylimidazolium and benzyldimethylimidazolium model compounds had a degradation of 55% and 46% at the same condition, respectively. The alkaline stability of three cations follows the order: benzyltrimethylammonium > benzyldimethylimidazolium > benzylmethylimidazolium. The NMR spectra and hydroxide conductivity change with immersing time in 1 M NaOH at 60 °C also confirmed that benzyltrimethylammonium functionalized polymer had a relative better alkaline stability than benzylmethylimidazolium and benzyldimethylimidazolium functionalized polymers in alkaline environment at elevated temperature. This research enriches the investigation on the alkaline stability of anion exchange membranes with quaternary ammonium, imidazolium and C2-substituted imidazolium.

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## Introduction

Intensive research efforts have been directed toward the development of anion exchange membranes (AEMs) for electrochemical applications in recently years. A major focus has been on the use of AEMs as a solid polymer electrolyte [1] and/or electrode binder in alkaline fuel cell [2] (AFC), primarily because it permits the use of inexpensive non-platinum-group metal electrocatalysts for the oxygen reduction reaction to greatly reduce the cost of fuel cell systems. As one of the key components in AFCs, AEMs could conduct the hydroxide or other anions from the cathode to the anode [3–6]. Currently, quaternary ammonium (QA) functionalized polymer electrolyte membranes have been most widely investigated as the candidate AEM materials. Various of polymers with tethered QA groups have been investigated, including radiation-grafted poly(vinylidene fluoride)s [7], poly(olefins) [8,9], poly(styrene)s [9,10], poly(phenylene oxide)s [11,12], poly(aryl ether ketone)s [13–16] and poly(aryl ether sulfone)s [16–18]. However, low conductivity is often observed for these alkaline AEMs when compared to acidic exchange membranes, due to the lower intrinsic mobility of the hydroxide ion. Great efforts have been devoted to addressing this issue via the following two strategies: (1) investigating new hydroxide conductive organic cations, such as imidazolium [19], phosphonium [20], guanidinium [21,22] and et al.; (2) precisely controlling the polymer architectures to achieve favorable phase-separated morphology, including preparing comb [23] or block copolymers [18,24], introducing spacer chain pendants and cross-linking. These efforts have promoted the AEMs to provide sufficient hydroxide conductivity for practical applications in fuel cells (higher than  $10^{-2}$  S  $\text{cm}^{-1}$ ).

Another major challenge with the practical applications of AEMs is their poor chemical stability in alkaline environments. The degradation of QA cations could occur under the working conditions (i.e. high pH above 60 °C) via the following pathways (i)  $\beta$ -hydrogen Hofmann elimination [25] ( $E_2$ ), (ii) direct nucleophilic substitution at an  $\alpha$ -carbon [26] ( $S_N2$ ), (iii) direct nucleophilic substitution at backbone arylene [27] ( $S_{Ar}$ ), or (iv) nitrogen ylide formation [28]. Each of these degradation pathways leads to a rapid loss of ion exchange capacity (IEC) and hence hydroxide conductivity. As one of the most interesting non-QA AEMs, imidazolium functionalized AEMs have been proposed for enhancing alkaline stability. They are expected to have a good stability in alkaline condition due to the five-membered heterocyclic ring and  $\pi$  conjugated structure of the imidazolium cations. The  $\pi$  conjugated structure help to delocalize positive charges, thus preventing nucleophilic attack by  $\text{OH}^-$  groups through Hofmann or  $S_N2$  elimination [29,30]. Surprisingly, there is a significant amount of starkly varying results and conflicting conclusions in the prior literature regarding the alkaline stability of imidazolium cations. Qiu et al. prepared the imidazolium and QA functionalized AEMs containing styrene and acrylonitrile components. The imidazolium functionalized membranes showed an excellent chemical stability of up to 1000 h without obvious loss of ion conductivity, whereas the membranes based on quaternary ammonium salts degraded in high pH solution [31]. Guo et al. also reported the imidazolium functionalized poly(styrene-co-

butyl methacrylate)s as AEM materials, which were stable even after 120 h in 6 M NaOH under 60 °C [32]. However, Zhang et al. investigated the identical imidazolium cations attached to polysulfone and found the decrease in mass and conductivity were 6.8% and 23.3% respectively after only 24 h in 3 M NaOH under 60 °C [33]. Varcoe et al. prepared a radiation-grafted AEM based on poly(ethylene-co-tetrafluoroethylene) (ETFE) containing pendent benzylmethylimidazolium head-groups, which was then compared to benzyltrimethylammonium functionalized ETFE at the same IEC. The imidazolium functionalized ETFE showed a similar ionic conductivity and much lower chemical stability than benzyltrimethylammonium-type AEMs in alkaline conditions. Recently, they also attached a modified imidazolium cations, of which the hydrogen at the C-2 position has been replaced by a methyl group, to the same radiation-grafted ETFE polymer. It was found to be more stable to alkaline treatment than the benzylmethylimidazolium-type AEM, but was still lower than the benzyltrimethylammonium-type AEM. The hydrolysis of the imidazolium cation under alkaline condition follows a ring-opening route by nucleophilic attack of  $\text{OH}^-$  groups on the acidic C-2 hydroxides. The methyl groups around the reactive C-2 position would hinder the nucleophilic attack by  $\text{OH}^-$ , thus improving the stability of the hydroxide form [6,34]. Sun et al. prepared 1,2-dimethylimidazolium-functionalized cross-linked alkaline anion exchange membranes and compared the stability of 1-methyl-3-(4-vinylbenzyl) imidazolium chloride and 1, 2-dimethyl-3-(4-vinylbenzyl) imidazolium chloride at 1M KOH 80 °C by NMR method. The NMR results show that 1, 2-dimethyl-3-(4-vinylbenzyl) imidazolium chloride is much more stable than 1-methyl-3-(4-vinylbenzyl) imidazolium chloride, indicating that 1,2-dimethylimidazolium has a significant advantage over C2-unsubstituted imidazolium in alkaline environment [35]. Lin et al. also investigated the alkaline stability of the same methyl-substituted imidazolium cations which were grafted to the poly(phenylene oxide) backbones [36]. The IEC did not change significantly after immersion in the aqueous KOH (2 mol  $\text{L}^{-1}$ ) solution at 25 °C even after 9 days of ageing. However, IEC decreased sharply to 40% and 50% for 7 and 9 days when the test temperature was increased to 60 °C. These observations was not consistent with the previous report of Yan et al., where polyfluorene-based AEMs containing methyl-substituted imidazolium cations were stable in aqueous KOH (1 mol  $\text{L}^{-1}$ ) at 60 °C for as long as 400 h [37]. Kim et al. also prepared the anion exchange membrane from commercial Parmax 1200 polymer focusing on the cation stability of the membranes. The Parmax imidazolium membrane showed better chemical stability than the quaternary ammonium functionalized polymers during its immersion in 1.0 M KOH at 60 °C over seven days. Alkaline Parmax polymer with the conjugated imidazole ring which is relatively strong against nucleophilic attack by hydroxide ions and thus could overcome the limitation of the quaternary ammonium hydroxide polymers [38]. To date, the investigations on the chemical stability of imidazolium or C2-substituted imidazolium functionalized polymers are insufficient and more detailed and comparative studies are required.

In the present work, a series of alkaline AEMs were prepared via bromomethylation of a poly(arylene ether ketone)

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