



Adamantammonium as a novel functional group for anion exchange membranes with excellent comprehensive performances



Jinlei Wang^a, Ying Chen^a, Qi Wei^a, Shanzhong Yang^a, Huagao Fang^a, Haibing Wei^{a, b, *}, Yunsheng Ding^{a, **}

^a Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei 230009, China

^b Research Center of Anhui Hualing Cable Group Company Limited, Wuhu 238371, China

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ABSTRACT

In the pursuit of alkali stable cation as functional group for anion exchange membranes (AEMs), a novel adamantammonium (AdA) cation, which replacing methyl group of conventional trimethylammonium by an adamantyl group, was synthesized and investigated. ¹H NMR spectroscopy was employed to quantify the extent of decomposition and the results showed that > 99% adamantammonium remaining after 7 days immersion in 2 M NaOH (in D₂O) at 80 °C. The AdA functionalized benzyl type poly(2,6-dimethyl phenylene oxide) polyelectrolytes, PPO-AdAs, were further prepared and characterized the AEM properties. Not only the chemical durability of these new PPO-AdA membranes, interestingly, but the conductivity and dimensional stability (water uptake and in-plane swelling) are superior to the benzylmethylammonium-benchmark PPO-based AEM (PPO-TMA). With the similar IEC values, the water uptake of PPO-AdA-41 sample is much lower than PPO-TMA-28, however, the conductivity of the former (15.7 mS cm⁻¹, chloride conductivity at 50 °C) is higher than the latter (13.3 mS cm⁻¹). Overall, the results of this study offer a base-stable cation, adamantammonium, and the corresponding adamantammonium-based AEMs for fuel cell applications with the advantages of chemical stability, enhanced conductivity and excellent dimensional stability as well as facial functionalization technique.

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1. Introduction

Owing to the advantages of high efficiency, high power density and low emissions, polymer electrolyte membrane fuel cell (PEMFC, also known as proton exchange membrane fuel cell) is considered to be one of the most promising clean energy sources for transportation and mobile power stations [1–3]. In the past two decades, PEMFC has been investigated intensively and moved forward to technologically maturation. However, a major catastrophic obstacle that prevents the broad commercialization of PEMFC is the high cost of platinum electro-catalysts. Alternatively, with the merit of independency on precious metal-based electro-catalyst, anion exchange membrane fuel cell (AEMFC) has attracted more

and more attention [4,5].

However, compared to the widely-accepted proton exchange membrane Nafion[®] (du Pont) utilized in PEMFC, there is no counterparts in AEMFC that can meet the requirements of durability and conductivity. Poor chemical stability and relatively low ionic conductivity of anion exchange membrane (AEM) are the main drawbacks for the practical fuel cell applications [5–8]. Compared to low ionic conductivity, which can be conquered by optimizing ionic transportation channels [9–13] and constructing micro/nanoporous in polymer matrix [14–16], the poor alkaline stability facing in AEM seems more chronic, especially at elevated temperatures. Therefore, recently, more efforts have been endeavored with the aim of developing highly stable AEM.

With the development of durable AEMs, in addition to the most studied quaternary ammonium (QA), numerous novel cations, such as quaternarized diazabicyclo[2.2.2]octane [17], imidazolium [18–25], guanidinium [26–29], phosphonium [30–32], sulfonium [33], pyrrolidinium [34], 1,2,3-triazolium [35] and piperidinium [36], have been investigated. However, because of the synthesis

* Corresponding author. Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, Anhui Key Laboratory of Advanced Functional Materials and Devices, Hefei University of Technology, Hefei 230009, China.

** Corresponding author.

E-mail addresses: hbwei@hfut.edu.cn (H. Wei), dingys@hfut.edu.cn (Y. Ding).

difficulty and the very different evaluation methodologies, the consensus among researchers that the superiority of cations' stability is difficult to achieve and these novel cations haven't been widely utilized in advanced AEMs. On the contrary, the traditional QA cations are extensively investigated and modified to adapt the stability requirements in AEM applications [37]. It is known that the trimethylammonium (TMA) group in benzyl type AEM itself has inferior alkaline stability and also can trigger the degradation of ether-containing polymer backbones [38,39], therefore, many efforts have been devoted to the improvement of the stability of TMA-based AEMs. Recently, more studies emphasized that trimethylammonium groups isolated from polymer backbone by a flexible alkyl chain not only significantly improved ionic conductivity of the membrane, but also alkaline stability. Although the β -protons existed as TMA linked to alkyl chain, Pivovar uncovered [40], by density functional theory calculations, that the concerns about Hofmann elimination could be lifted when the carbon atoms in the alkyl chains extended to four. Jannasch and his coworkers [41] comparatively studied the alkaline stability of PPO-based AEMs with trimethylammonium moiety located in benzylic positions and attached *via* heptyl side chains. By analysis the ^1H NMR signal changes, after 4-day immersion in 1 M NaOH (aq) at 80 °C, they found that almost no degradation detected in side chain type AEM, while only 50% TMA remained for the corresponding benzyl type AEM. More recently, they reported that cycloaliphatic QAs (quaternary piperidinium) tethered to PPO backbone *via* heptyl spacers also exhibited good chemical stability [36]. Hickner et al. [13] reported that the conductivity of PPO with fluorene side chains with pendent TMA groups degraded 17.6% after 1000 h aging in 1 M NaOH at 80 °C, however, the counterparts with benzyl-trimethylammonium cations lost 60% of its initial conductivity. Apart from heptyl spacer, other flexible spacers also studied. Xu and co-workers [42] reported that only 10% decline in conductivity after 7 days alkaline hydrolysis in 1 M NaOH at 60 °C when TMA group separated from PPO backbone by phenylpropyl spacer. Nonetheless, the preparation of side chain AEM needs particular synthesis skills, for example, the synthesis of their precursor haloalkylated polymers involved strict water and oxygen free conditions.

Considering the preparation simplicity and low cost, it is intriguing to develop benzyl type AEM with acceptable alkaline stability by traditional Menshutkin reaction. However, attempts to modify the traditional benzyltrimethylammonium to benzalkonium, such as benzyl-1-azonia-4-azabicyclo-[2,2,2]-octane and benzyl tri-*n*-butylammonium groups [43], in order to overcome the alkaline instability, seem unsuccessful and designing the alkaline stable benzalkonium suitable to AEM applications is a real challenge.

Herein, inspired by adamantane with rigid spherical cycloaliphatic-cage structure and strong hydrophobic nature, we scrutinize the stability of benzyl-adamantammonium cation and the corresponding AEM properties after appended it to polymer architectures. We hypothesized that by replacing methyl to a rigid adamantyl group, the steric hindrance of trimethylammonium would increase a lot against hydroxide anion attacking and improves the membrane stability. Moreover, the introduction of adamantyl group with rigid cage structure could increase the free volume inside the polymer matrix, which may favor the enhancement of ionic conductivity.

2. Experimental section

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was kindly supplied by Saudi Basic Industries Corporation. *N*-bromosuccinimide

(NBS) were purchased from Aladdin Industrial Corporation and used without further purification. 2,2'-Azobisisobutyronitrile (AIBN, Sinopharm Chemical Reagent Co., Ltd, AR) was recrystallized from ethanol and stored in refrigerator. *N*-methyl-2-pyrrolidone (NMP, Sinopharm Chemical Reagent Co., Ltd, AR) were purified by distillation under vacuum before use. 1-Adamantylamine, 2,2,2-trifluoroethanol and paraformaldehyde were purchased from Energy Chemical and used as received. Unless otherwise noted, the other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2. Synthesis of *N,N*-dimethyl-*N*-benzyladamantammonium(DMBAdA) bromide

1-(*N,N*-dimethylamino)adamantane (2.3 mmol, 0.40 g, which was successfully synthesized according to the literature [44] using amantadine, paraformaldehyde and NaBH_4 in the solvent of 2,2,2-trifluoroethanol), benzyl bromide (3.4 mmol, 0.58 g) and 5 mL chloroform were added to a 25 mL round-bottomed flask equipped with a magnetic stirrer. The mixture was stirred for 24 h at 50 °C. After cooling, the solvent was removed under vacuum, and the residual solid was washed thoroughly with ethyl acetate for several times. The white products were filtered and dried under vacuum at 60 °C for 24 h with the yield of 93% (0.73 g).

^1H NMR (600 MHz, D_2O) δ 1.69–1.78 (q, 6H), 2.12 (s, 6H), 2.37 (s, 3H), 2.77 (s, 6H), 4.41 (s, 2H), 7.54 ppm (m, 5H); ^{13}C NMR (150 MHz, CD_3OD) δ 32.0, 36.0, 36.1, 43.9, 61.8, 76.8, 129.3, 130.0, 131.4, 134.7 ppm; HRMS: (ESI) calcd for $(\text{C}_{19}\text{H}_{28}\text{N})^+$ (M^+) 270.2216; found 270.2167.

2.3. Synthesis of adamantammonium functionalized PPO (PPO-AdA)

The typical procedure, take PPO-AdA-41 as an example, was illustrated as follows:

A 100 mL round bottomed flask equipped with a magnetic stirrer was charged with 0.5 g (1.3 mmol benzylic bromide) PPO-Br-41 (prepared according to the literature [45], brominated PPO with the degree of bromination of 41%) and NMP (10 mL). The mixture was stirred at room temperature until a homogeneous solution was formed, then 1-(*N,N*-dimethylamino)adamantane (0.38 g, 2.1 mmol) was added and the reaction mixture was warmed at 50 °C during 48 h under stirring. After cooling to the room temperature, the mixture was added dropwise to diethyl ether to precipitate the product. After washed thoroughly with diethyl ether and dried under vacuum, the product (PPO-AdA-41) was obtained as a light brown powder (0.69 g, yield: 93%).

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ 1.59 (m, 6H), 2.03–2.20 (m, 18.4H), 2.79 (s, 5.2H), 4.21 (s, 1.7H), 6.51–7.49 ppm (m, 4.8 H).

2.4. Casting of PPO-AdA membranes and ion exchange

The PPO-AdA AEMs with the counter ion of Br^- was prepared by solution casting from NMP solution. Take the preparation of PPO-AdA-41 membrane as an example: dissolve 0.5 g dry PPO-AdA-41 powder samples in the Br^- form in 5 mL NMP to yield a ~10% solution. After filtered through a glass filter, the solution was casted onto a glass plate, dried at 80 °C for overnight, and followed by an additional further drying in vacuum oven for another 12 h at 80 °C. The resultant membrane was soaked in deionized water and peeled off the glass to obtain the PPO-AdA-41 membrane with the counter ion of Br^- form. The membrane's thickness was in the range of 30–50 μm . The chloride form membrane was obtained by exchanging the bromide form membrane in 2 M aqueous NaCl for 24 h followed by fresh 2 M NaCl (aq) for another 24 h, then

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